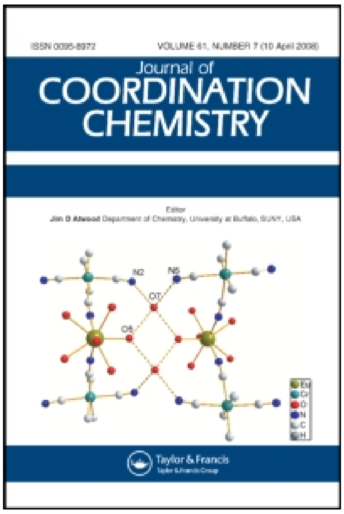

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Synthesis, Characterization and Third-Order Nonlinear Optical Properties of a Series of Ruthenium(II) Complexes Containing 2-Arylimidazo-[4,5- f][1,10]Phenanthroline

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SYNTHESIS, CHARACTERIZATION AND THIRD-ORDER NONLINEAR OPTICAL PROPERTIES OF A SERIES OF RUTHENIUM(II) COMPLEXES CONTAINING 2-ARYLIMIDAZO-[4,5-*f*][1,10]PHENANTHROLINE

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Three novel mononuclear ruthenium(II) complexes $[Ru(dmp)_2L]^{2+}$ [dmp = 2,9-dimethyl-1,10-phenanthroline, L = 2-phenylimidazo-[4,5-*f*][1,10]phenanthroline (PIP), 2-(4′-hydroxyphenyl)imidazo-[4,5-*f*][1,10]phenanthroline (HOP), 2-(4′-dimethylaminophenyl)imidazo-[4,5-*f*][1,10]phenanthroline (DMNP)] were synthesized and characterized by ES-MS, ^{1}H NMR, UV–Vis and electrochemistry. The nonlinear optical (NLO) properties of the ruthenium(II) complexes were investigated by Z-scan techniques with 12 ns laser pulses at 540 nm, and all of them exhibit both NLO absorption and self-defocusing effects. The corresponding effective NLO susceptibility $|\chi^3|$ of the complexes is in the range of 5.15×10^{-12}–6.34×10^{-12} esu.

Keywords: Ruthenium(II) complex; Polypyridine ligand; Nonlinear optical properties

INTRODUCTION

In recent years organometallic and coordination complexes have emerged as potential building blocks for nonlinear optical (NLO) materials [1–6]. Compared to organic molecules, metal complexes can have a larger variety of structures and a much greater diversity of tunable electronic properties by virtue of the coordinating metal center. However, the vast majority of such studies have focused on quadratic optical nonlinearities and, to a far lesser extent, on third-order responses. Their vast potential as the third-order NLO materials remains therefore largely untapped.

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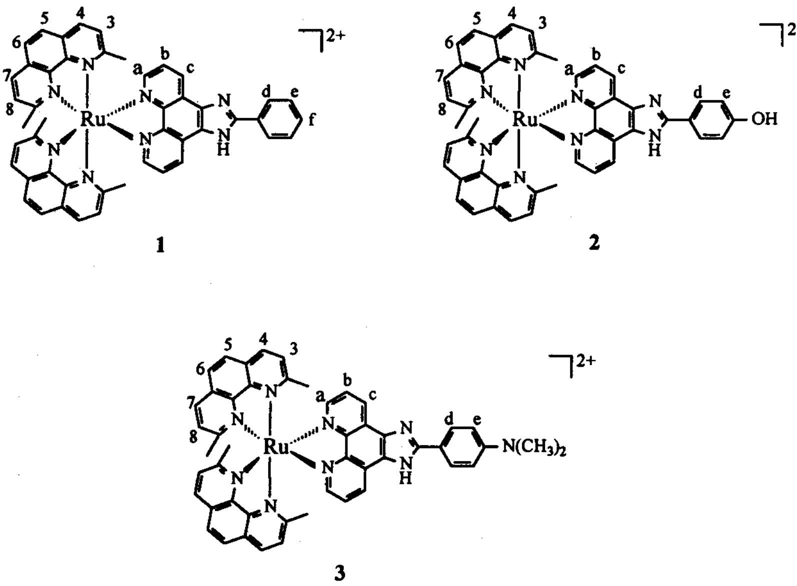

SCHEME 1 Structures of the ruthenium(II) complexes.

Ruthenium(II) polypyridine complexes are excellent photosensitizers for artificial photosynthetic systems as well as for optoelectronic applications due to their rich photochemical behavior and diversity of coordination forms [7]. In our previous study, we have found that ruthenium(II) complexes containing 2-phenylimidazo[4,5-*f*][1,10]phenanthroline derivatives show large third-order NLO effects [8–10]. Here we describe the syntheses of several new ruthenium(II) polypyridine complexes $[Ru(dmp)_2L]^{2+}$ [dmp = 2,9-dimethyl-1,10-phenanthroline, L = 2-phenylimidazo-[4,5-*f*][1,10]phenanthroline (PIP), 2-(4′-hydroxy-phenyl)-phenylimidazo-[4,5-*f*]1,10] phenanthroline (HOP), 2-(4′-dimethylaminophenyl)-phenylimidazo-[4,5-*f*][1,10]phenanthroline (DMNP)] (Scheme 1). Their photophysical, electrochemical and third-order NLO properties have been studied.

EXPERIMENTAL

Chemicals

The compounds PIP [11], HOP [12], DMNP [13] and *cis*-$[Ru(dmp)_2Cl_2] \cdot 2H_2O$ [14] were synthesized according to literature methods. Other materials were commercially available and of reagent grade.

Preparations of Complexes

Caution! Perchlorate complexes are potential explosives. These complexes must be handled in small quantity and with great care.

$[Ru(dmp)_2\ (PIP)](ClO_4)_2 \cdot H_2O$ (1)

A mixture of *cis*-$[Ru(dmp)_2Cl_2] \cdot 2H_2O$ (0.5 mmol, 0.31 g), PIP (0.5 mmol, 0.15 g) and ethanol (30 mL) was refluxed under argon for 6 h during which the solution color changed from purple to red. The solution was cooled to room temperature. After filtration, a red precipitate was obtained by dropwise addition of aqueous $NaClO_4$ solution. The product was purified by column chromatography on alumina using acetonitrile–toluene (2 : 1, v/v) as eluent. The mainly red band was collected. The solvent was removed under reduced pressure and then dried *in vacuo*. Yield 67.8%. Anal. Calcd. for $C_{47}H_{36}Cl_2N_8O_8Ru \cdot H_2O$(%): C, 54.8; H, 3.7; N, 10.9. Found: C, 54.4; H, 3.7; N, 10.8. ESMS [CH_3OH, *m*/*z*]: 813 ($[M-2ClO_4-H]^+$), 407 ($[M-2ClO_4]^{2+}$). ^1H NMR [500 MHz, $(CD_3)_2SO$]: δ 8.92 (d, 2H, $J=8.5$), 8.87 (d, 2H, $J=8$), 8.45 (d, 2H, $J=8$), 8.43 (d, 2H, $J=8.5$), 8.25 (d, 2H, $J=5$), 8.23 (d, 2H, $J=5$), 7.98 (d, 2H, $J=8.5$), 7.61 (t, 2H, $J=7.5$), 7.55 (t, 2H, $J=7$), 7.37 (d, 2H, $J=8.5$), 7.24 (t, 1H, $J=6$), 7.15 (d, 2H, $J=8$), 1.95 (s, 6H), 1.71 (s, 6H).

$[Ru(dmp)_2(HOP)](ClO_4)_2 \cdot 2H_2O$ (2)

This red complex was synthesized in an identical manner to that described for Complex **1** with HOP in place of PIP. Yield 65.8%. Anal. Calcd. for $C_{47}H_{36}N_8O_9Cl_2Ru \cdot 2H_2O$(%): C, 53.0; H, 3.8; N, 10.5%. Found: C, 53.3; H, 3.7; N, 10.2. ESMS [CH_3OH, *m*/*z*]: 829 ($[M-2ClO_4-H]^+$), 415 ($[M-2ClO_4]^{2+}$). ^1H NMR [500 MHz, $(CD_3)_2SO$]: δ 9.86 (s, 1H), 8.90 (d, 2H, $J=8.5$), 8.87 (d, 2H, $J=8.5$), 8.46 (d, 2H, $J=8$), 8.43 (d, 2H, $J=8$), 8.24 (d, 2H, $J=9$), 8.11 (d, 2H, $J=8.5$), 7.97 (d, 2H, $J=8.5$), 7.44 (dd, 2H, $J_1=5.5$ and $J_2=3$), 7.37 (d, 2H, $J=8$), 7.27 (d, 2H, $J=5$), 6.92 (d, 2H, $J=9$), 1.95 (s, 6H), 1.72 (s, 6H).

$[Ru(dmp)_2(DMNP)](ClO_4)_2 \cdot 2H_2O$ (3)

This red complex was synthesized in an identical manner to that described for Complex **1** with DMNP in place of PIP. Yield 67.8%. Anal. Calcd. for $C_{49}H_{41}N_9O_8Cl_2Ru \cdot 2H_2O$(%): C, 53.9; H, 4.2; N, 11.5. Found: C, 53.6; H, 3.9; N, 11.2. ESMS [CH_3OH, *m*/*z*]: 856 ($[M-2ClO_4-H]^+$), 429 ($[M-2ClO_4]^{2+}$). ^1H NMR [500 MHz, $(CD_3)_2SO$]: δ 8.91 (d, 2H, $J=8.5$), 8.86 (d, 2H, $J=8$), 8.45 (d, 2H, $J=8$), 8.43 (d, 2H, $J=9$), 8.24 (d, 2H, $J=9$), 8.05 (d, 2H, $J=7$), 7.97 (d, 2H, $J=8.5$), 7.48 (m, 2H), 7.37 (d, 2H, $J=8.5$), 7.17 (d, 2H, $J=8.5$), 6.89 (d, 2H, $J=8.5$), 3.29 (s, 6H), 1.95 (s, 6H), 1.71 (s, 6H).

Physical Measurements

The microanalyses (C, H and N) were carried out with a Perkin-Elmer 240Q elemental analyser. UV–Vis spectra were recorded on a Shimadzu UV-3101PC spectrophotometer. ^1H NMR spectra were measured on a Varian-500 NMR spectrometer with d^6-DMSO as solvent at room temperature and all chemical shifts are given relative to TMS. Electrospray mass spectra (ES-MS) were recorded on a LCQ system (Finnigan MAT, USA) using methanol as the mobile phase. The spray voltage, tube lens offset, capillary voltage and capillary temperature were set at 4.50 kV, 30.00 V, 23.00 V and 200°C, respectively, and the quoted *m*/*z* values are for the major peaks in the isotope distribution.

Cyclic voltammetric measurements were performed on an EG&G PAR 273 polarographic analyser and 270 universal programmer. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate in acetonitrile freshly distilled twice from phosphorus pentaoxide and deaerated by purging with nitrogen for 0.5 h. A standard three-electrode system was used comprising a platinum microcylinder working electrode, platinum-wire auxiliary electrode and a saturated calomel reference electrode (SCE).

Third-Order Nonlinear Optical Property Measurement

The DMF solutions 5.0×10^{-5} M in ruthenium complexes were placed in a 2 mm quartz cuvette for optical measurements. Their nonlinear refraction and nonlinear absorption were measured with a 12 ns pulsed laser at 540 nm as described in the literature [8–10].

RESULTS AND DISCUSSION

Synthesis and Characterization

The mixed-ligand complexes are prepared by direct reaction of $Ru(dmp)_2Cl_2$ with the appropriate ligands in ethanol in relatively high yield. The desired ruthenium(II) complexes were isolated as the perchlorates and purified by column chromatography. In the ES-MS spectra for the complexes, only the signals $[M - 2ClO_4 - H]^+$ and $[M - 2ClO_4]^{2+}$ were observed. The measured molecular weights were consistent with expected values.

All the ruthenium(II) complexes give well-defined ^1H NMR spectra (Fig. 1). The proton chemical shifts were assigned with the aid of ^1H-^1H COSY experiments and by comparison with those of similar compounds [11,12,15–17]. In the complexes the two dmp ligands and the two halves of L (L = PIP, HOP or DMNP) are chemically and magnetically equivalent. However, the two halves of each dmp are not, due to the distinct shielding influences of the adjacent dmp and L, leading to eight signals corresponding to the dmp protons: one set of four is associated with the half of dmp near the L, the other set of four is associated with the half of dmp near the other dmp. Since the shielding effect of L is obviously greater than that of dmp, the chemical shifts of the latter protons are greater than those of the former. In addition, the proton resonance on the nitrogen atom of the imidazole ring was not observed, because the proton is active and exchanges quickly between the two nitrogens of the imidazole ring. A similar example has been reported previously [11].

Electrochemical Studies

The electrochemical data for all complexes are listed in Table I. Each complex exhibits oxidation (one) and reduction (two or three) waves in the sweep range −1.90 to +1.80 V (Fig. 2). The electrochemical behavior of the ruthenium(II) polypyridyl complex has been rationalized in terms of a metal-based oxidation and a series of reductions which are ligand-based occurring in a stepwise manner for each π^* system [18]. As expected, replacement of an H atom in PIP by electron-donating groups shifts the Ru(II)/Ru(III) oxidation to the negative. These data are consistent with the electron donors stabilizing the Ru(III) via raising the absolute energy of the highest occupied

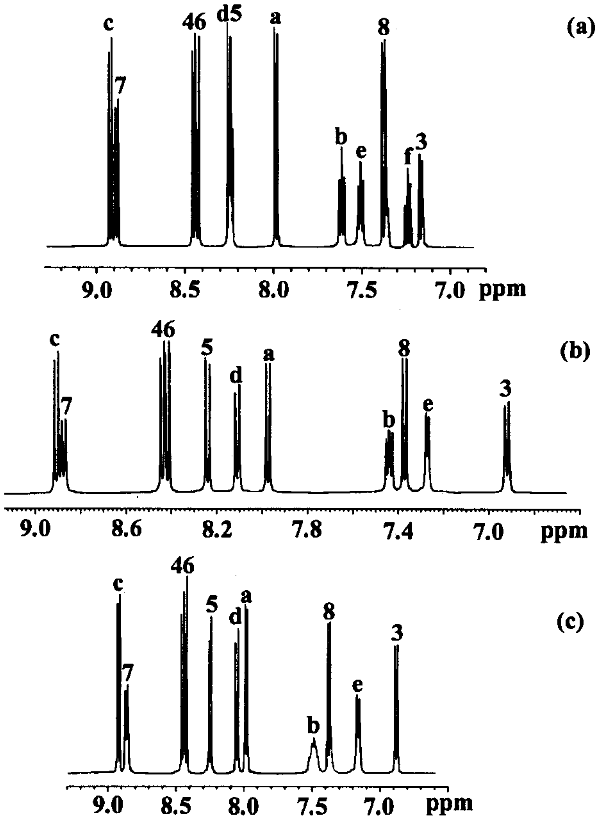

FIGURE 1 ^{1}H NMR spectra of: (a) $[Ru(dmp)_2(PIP)]^{2+}$; (b) $[Ru(dmp)_2(HOP)]^{2+}$; and (c) $[Ru(dmp)_2(DMNP)]^{2+}$ in the aromatic region between $\delta = 6.7$ and $\delta = 9.2$ ppm [$(CD_3)_2SO$ solvent, TMS reference].

TABLE I Electrochemical and absorption data of the ruthenium(II) complexes

Complex	*$E_{1/2}/V$ vs SCE*[a]				λ_{max}/nm^b (ε/M^{-1} cm^{-3})
	$Ru^{II/III}$	*Ligand reduction*			
1	+1.30	−1.00	−1.33	−1.53	470 (13500), 265 (95100)
2	+1.28	−1.10	−1.36	−1.59	472 (17000), 442 (sh), 269 (100500)
3	+1.25	−1.22	−1.43	−1.66	476 (14000), 352 (35800), 270 (71100)

[a] All complexes were measured in 0.1 M NBu_4ClO_4–MeCN, error in potentials was ±0.02 V; $T = 23 \pm 1$°C; scan rate = 100 mV s^{-1}; [b] In DMF.

molecular orbital (HOMO) [19–21]. With reference to previous studies on similar systems [8,11,17], the first reduction, which is usually controlled by the ligand having the most stable lower unoccupied molecular orbital (LUMO), is assigned to a reduction centered on the 2-arylimidazo[4,5-*f*][1,10]phenanthroline.

Optical Response

The absorption spectra of the complexes were recorded in DMF (Fig. 3) and results are presented in Table II. The Complexes **1–3** all show intense ligand-centered transitions

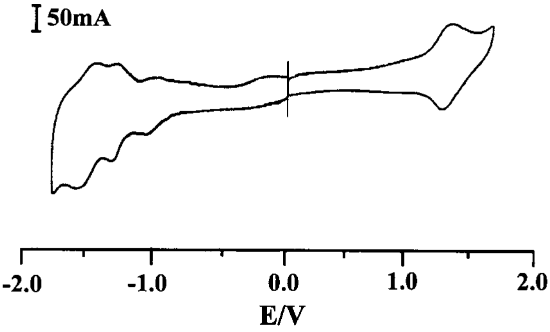

FIGURE 2 Cyclic voltammogram of $[Ru(dmp)_2(PIP)]^{2+}$ in acetonitrile.

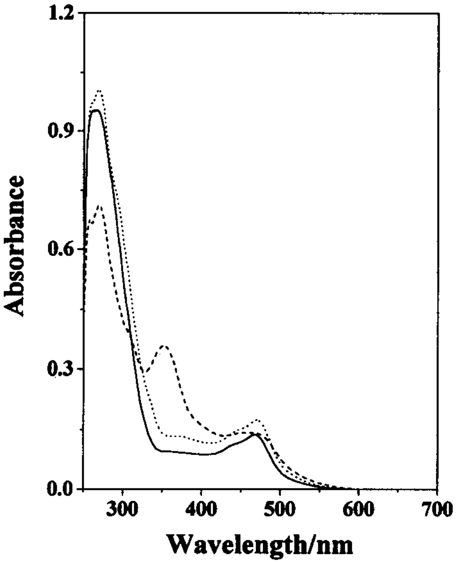

FIGURE 3 Absorption spectra of $[Ru(dmp)_2(PIP)]^{2+}$ (full line), $[Ru(dmp)_2(HOP)]^{2+}$ (dot line) and $[Ru(dmp)_2(DMNP)]^{2+}$ (dash line) in DMF at room temperature.

TABLE II Measurement results of the Ru^{II} complexes using Z-scan techniques

Complex	$\Delta T_{v\text{-}p}$	I_0 (W m^{-2})	α (cm^{-1})	n_2 (m^2 W^{-1})	α_2 (m W^{-1})	$\chi^{(3)}$ (esu[a])	γ (esu[a])
1	0.204	2.13×10^{12}	0.95	-1.30×10^{-17}	5.47×10^{-11}	5.15×10^{-12}	5.15×10^{-29}
2	0.209	1.93×10^{12}	1.18	-1.51×10^{-17}	7.77×10^{-11}	6.03×10^{-12}	6.03×10^{-29}
3	0.214	1.99×10^{12}	1.40	-1.54×10^{-17}	12.10×10^{-11}	6.34×10^{-12}	6.34×10^{-29}

[a] Values ± 10%.

in the UV region and metal-to-ligand charge transfer (MLCT) transitions in the visible region. The low-energy bands at 470, 472 and 476 nm for Complexes **1**, **2** and **3**, respectively, are assigned as MLCT $Ru(d\pi) \rightarrow L(\pi^*)$ transitions [L = PIP, HOP and DMNP]. In addition, a unique band at 352 nm is exhibited in the absorption spectrum of Complex **3**, which can be assigned to the intraligand (IL) transition of DMNP.

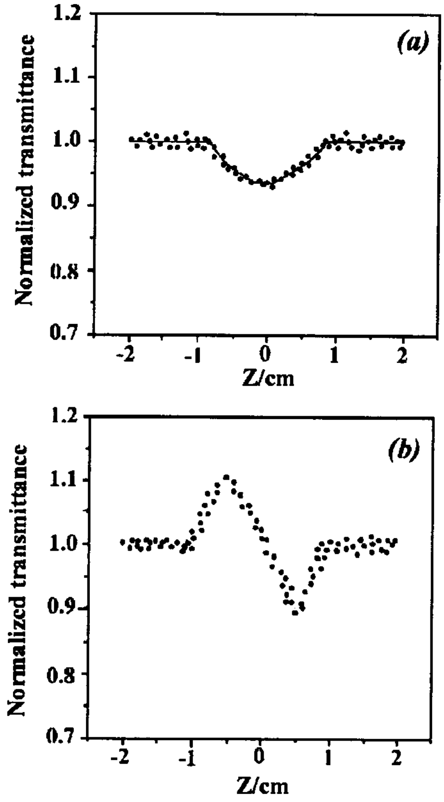

FIGURE 4 Z-scan data (filled circles) of 5×10^{-5} M of $[Ru(dmp)_2(PIP)][ClO_4]_2 \cdot 2H_2O$, at 540 nm with $I(Z=0)$ being 2.13×10^{12} W/m^2: (a) collected under open aperture configuration showing NLO absorption. The solid curve is a theoretical fit based on Eqs (1) and (2); (b) obtained by dividing the normalized Z-scan data obtained under closed aperture configuration by the normalized Z-scan data in (a). It shows a self-defocusing effect of the complex.

The NLO properties of Complexes **1–3** were investigated with 540 nm laser pulses of 12 ns duration in 5.0×10^{-5} M DMF solutions. To obtain the NLO parameters, we employed a Z-scan theory that considers an effective nonlinearity of third-order nature [22,23]. The nonlinear absorption components of Complexes **1–3** were evaluated by Z-scan experiment under an open aperture configuration (Fig. 4a). The nonlinear refractive properties of the ruthenium(II) complexes were assessed by dividing the normalized Z-scan data obtained under the closed-aperture configuration by the normalized Z-scan data obtained under the open-aperture configuration (Fig. 4b).

In accordance with the α_2 and n_2 values, the modulus of the effective third order susceptibility $\chi^{(3)}$ and the corresponding modulus of the hyperpolarizability γ can be calculated [24]. Table II lists the results for the ruthenium(II) complexes.

From the discussions above, we can reasonably state that Complexes **1–3** have similar NLO properties, exhibiting, strong self-defocusing performance and reverse saturable absorption. The origins of these good NLO properties can be attributed to the excited state absorption, two-photon absorption, third-order bound-electronic effect and nonlinear scattering [25–27]. The $|\gamma|$ values obtained for the new complexes may be compared with some known NLO chromophores (5.6×10^{-35}–8.6×10^{-34} esu for Group 10 metal alkynyl polymers at 1064 nm [28], 2.27×10^{-32} esu for an alkynylruthenium dendrimer at 800 nm [29], 1.6×10^{-28} esu for a half-open cubane-like $[WOS_3(CuBr)_3(\mu_2\text{-}Br)]^{3-}$ at 532 nm [30]). Inspection of $|\gamma|$ (1 cf. 2 cf. 3) reveals an increase in this parameter, which can be attributed to the incorporation of electron-donating groups on the ligand PIP, resulting in higher electron delocalization of the π-system and, in turn, enhancement of NLO effects.

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