# Bis(4,4'-dimethyl-2,2'-bipyridine)ruthenium(II) Complexes Containing 2-Arylimidazo-[4,5-*f*][1,10]phenanthroline: Syntheses, Characterization and Third-order Nonlinear Optical Properties[†]

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Four novel mononuclear ruthenium(II) complexes [Ru(dmb)$_2$L]$^{2+}$ [dmb = 4,4'-dimethyl-2,2'-bipyridine, L = imidazo-[4,5-*f*][1,10]phenanthroline (IP), 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 properties of the ruthenium(II) complexes were investigated by Z-scan techniques with 12 ns laser pulse at 540 nm, and all of them exhibit both nonlinear optical (NLO) absorption and self-defocusing effect. The corresponding effective NLO susceptibility $|\chi^3|$ of the complexes is in the range of $2.68 \times 10^{-12}$—$4.57 \times 10^{-12}$ esu.

**Keywords**    ruthenium(II) complex, polylpyridine ligand, nonlinear optics

## Introduction

Organometallic and coordination complexes have recently emerged as potential building blocks for nonlinear optical (NLO) materials.[1-6] Compared with 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 has been 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.

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 studies, we have found that ruthenium(II) complexes containing 2-phenylimidazo-[4,5-*f*]-[1,10]phenanthroline derivatives show large third-order NLO effects.[8-11] In order to further explore this promising kind of complexes, and also to assess the structure-property relationships that govern third-order NLO polarization, we have synthesized four ruthenium(II) polypyridine complexes [Ru(dmb)$_2$L]$^{2+}$ [dmb = 4,4'-dimethyl-2,2'-bipyridine, L = imidazo-[4,5-*f*][1,10]phenanthroline (IP), 2-phenylimidazo-[4,5-*f*][1,10]phenanthroline (PIP), 2-(4'-hydroxyphenyl)imidazo-[4,5-*f*][1,10]phenanthro-

line (HOP), 2-(4'-dimethylaminophenyl)imidazo-[4,5-*f*][1,10]phenanthroline (DMNP)] (Scheme 1). Their-photophysical, electrochemical and third-order NLO properties have been studied.

## Experimental

### Chemicals

The compounds IP,[12] PIP,[12] HOP,[13] DMNP[14] and *cis*-[Ru(dmb)$_2$Cl$_2$]·2H$_2$O[15] were synthesized according to reported methods. Other materials were commercially available and of reagent grade.

### Synthesis of [Ru(dmb)$_2$(IP)](ClO$_4$)$_2$ (1)

A mixture of *cis*-[Ru(dmb)$_2$Cl$_2$]·2H$_2$O (0.19 mmol, 0.10 g), IP (0.2 mmol, 0.05 g) and methanol (20 mL) was refluxed under argon for 6 h during which the solution color changed from purple to red. The methanol was evaporated to dryness, the solid was taken up in H$_2$O, and the mixture was filtered to remove unre-

acted ligand, a red precipitate was obtained by dropwise addition of a saturated aqueous NaClO$_4$ solution. The product was purified by column chromatography on alumina using acetonitrile-toluene (2:1, $V/V$) as eluent and then dried *in vacuo*. Yield 0.14 g, 82%, UV-vis (CH$_3$CN) $\lambda_{max}$: 462, 327, 284, 251 nm; $^1$H NMR ((CD$_3$)$_2$SO, 500 MHz) $\delta$: 8.91 (d, $J = 8$ Hz, 2H, H$_c$), 8.72 (s, 2H, 3'-H), 8.67 (s, 2H, 3-H), 8.36 (s, 1H, H$_d$), 7.88 (d, $J = 5$ Hz, 2H, H$_a$), 7.77 (dd, $J_1 = 5.5$ Hz, $J_2 = 3$ Hz, 2H, H$_b$), 7.67 (d, $J = 5.5$ Hz, 2H, 6'-H), 7.40 (d, $J = 6$ Hz, 2H, 6-H), 7.36 (d, $J = 6$ Hz, 2H, 5'-H), 7.15 (d, $J = 6$ Hz, 2H, 5-H), 2.55 (s, 6H, 4'-CH$_3$), 2.49 (s, 6H, 4-CH$_3$); ESMS (CH$_3$OH) $m/z$: 688 ([M − 2ClO$_4$ − H]$^+$), 345 ([M − 2ClO$_4$]$^{2+}$). Anal. calcd for C$_{37}$H$_{32}$-Cl$_2$N$_8$O$_8$Ru·2H$_2$O: C 47.89, H 3.45, N 12.08; found C 47.58, H 3.51, N 11.86.

### Synthesis of [Ru(dmb)$_2$(PIP)](ClO$_4$)$_2$ (2)

This complex (red) was synthesized in an identical

**Scheme 1**    Structures of the ruthenium(II) complexes



1



2



3



4
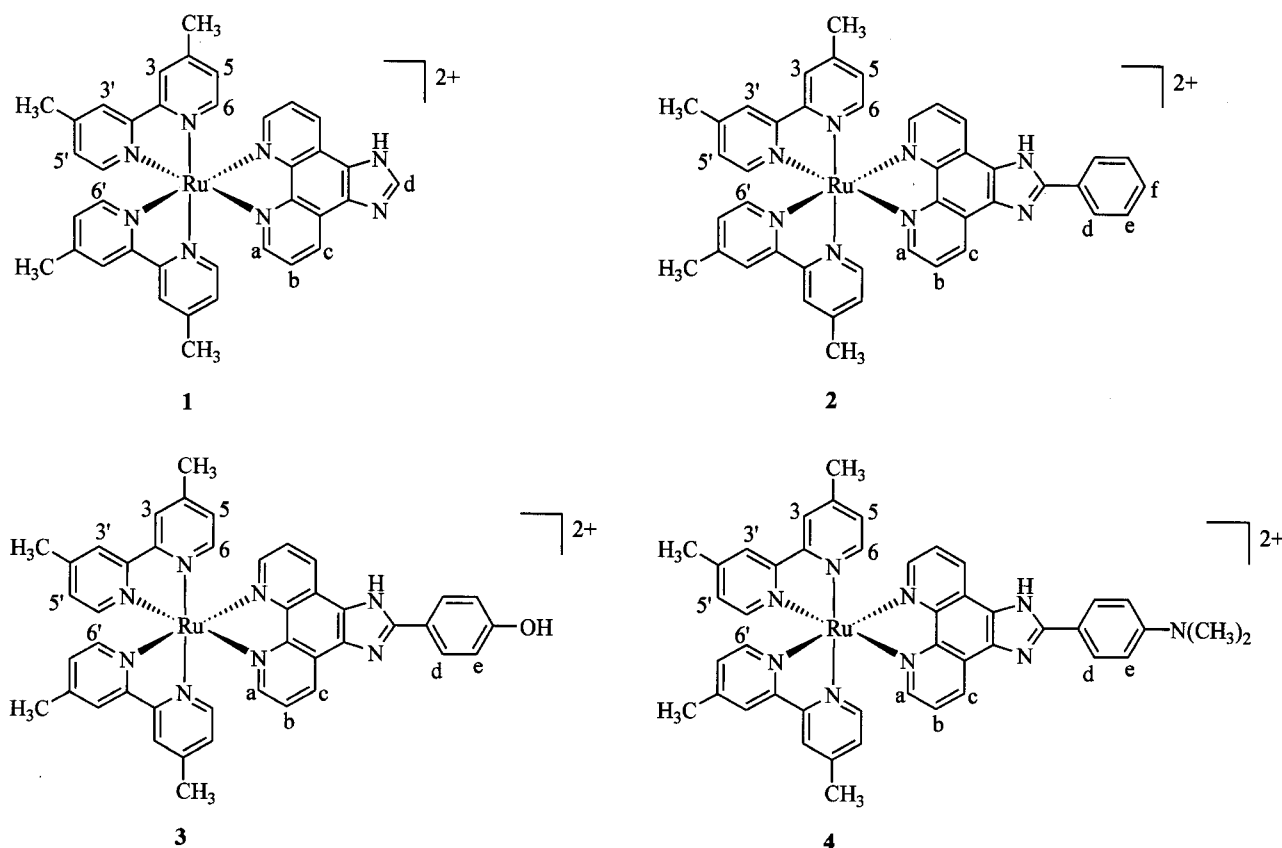
manner to that described for complex **1** with PIP in place of IP. Yield 0.15 g, 84.5%, UV-vis ($CH_3CN$) $\lambda_{max}$: 465, 334, 287, 249 nm; $^1H$ NMR (($CD_3$)$_2$SO, 500 MHz) $\delta$: 9.01 (d, $J = 8$ Hz, 2H, $H_c$), 8.72 (s, 2H, 3'-H), 8.68 (s, 2H, 3-H), 8.38 (d, $J = 8$ Hz, 1H, $H_d$), 7.89 (d, $J = 4$ Hz, 2H, $H_a$), 7.78 (dd, $J_1 = 5$ Hz, $J_2 = 3$ Hz, 2H, $H_b$), 7.68 (d, $J = 5.5$ Hz, 2H, 6'-H), 7.52 (t, $J = 8$ Hz, 2H, $H_e$), 7.48 (t, $J = 7.5$ Hz, 1H, $H_f$), 7.41 (d, $J = 5.5$ Hz, 2H, 6-H), 7.39 (d, $J = 6$ Hz, 2H, 5'-H), 7.17 (d, $J = 6$ Hz, 2H, 5-H), 2.55 (s, 6H, 4'-$CH_3$), 2.49 (s, 6H, 4-$CH_3$); ESMS ($CH_3OH$) $m/z$: 764 ([$M - 2ClO_4 - H$]$^+$), 383 ([$M - 2ClO_4$]$^{2+}$). Anal. calcd for $C_{43}H_{36}Cl_2N_8O_8Ru \cdot H_2O$: C 50.53, H 3.72, N 10.97; found C 50.16, H 3.90, N 10.82.

*Synthesis of* [$Ru(dmb)_2(HOP)$]($ClO_4$)$_2$ (**3**)

This complex (red) was synthesized in an identical manner to that described for complex **1** with HOP in place of IP. Yield 0.13 g, 68%, UV-vis ($CH_3CN$) $\lambda_{max}$: 466, 287 nm; $^1H$ NMR (($CD_3$)$_2$SO, 500 MHz) $\delta$: 10.04 (s, 1H, OH), 9.09 (d, $J = 8$ Hz, 2H, $H_c$), 8.73 (s, 2H, 3'-H), 8.69 (s, 2H, 3-H), 8.19 (d, $J = 8.5$ Hz, 2H, $H_d$), 8.03 (d, $J = 4.5$ Hz, 2H, $H_a$), 7.89 (dd, $J_1 = 5$ Hz, $J_2 = 3$ Hz, 2H, $H_b$), 7.66 (d, $J = 6$ Hz, 2H, 6'-H), 7.41 (d, $J = 6$ Hz, 2H, 6-H), 7.39 (d, $J = 6$ Hz, 2H, 5'-H), 7.15 (d, $J = 6$ Hz, 2H, 5-H), 7.00 (d, $J = 8.5$ Hz, 2H, $H_e$), 2.55 (s, 6H, 4'-$CH_3$), 2.49 (s, 6H, 4-$CH_3$); ESMS ($CH_3OH$) $m/z$: 780 ([$M - 2ClO_4 - H$]$^+$), 391 ([$M - 2ClO_4$]$^{2+}$). Anal. calcd for $C_{43}H_{36}Cl_2N_8O_9Ru \cdot H_2O$: C 49.75, H 3.47, N 10.80; found C 50.01, H 3.25, N 10.94.

*Synthesis of* [$Ru(dmb)_2(DMNP)$]($ClO_4$)$_2$ (**4**)

This complex (red) was synthesized in an identical manner to that described for complex **1** with DMNP in place of IP. Yield 0.11 g, 56%, UV-vis ($CH_3CN$) $\lambda_{max}$: 463, 345, 286, 246 nm; $^1H$ NMR (($CD_3$)$_2$SO, 500 MHz) $\delta$: 9.05 (d, $J = 8.5$ Hz, 2H, $H_c$), 8.72 (s, 2H, 3'-H), 8.68 (s, 2H, 3-H), 8.17 (d, $J = 7$ Hz, 2H, $H_d$), 7.99 (d, $J = 7$ Hz, 2H, $H_a$), 7.85 (dd, $J_1 = 5$ Hz, $J_2 = 3$ Hz, 2H, $H_b$), 7.66 (d, $J = 6$ Hz, 2H, 6'-H), 7.41 (d, $J = 5.5$ Hz, 2H, 6-H),

7.38 (d, $J = 6$ Hz, 2H, 5'-H), 7.15 (d, $J = 6$ Hz, 2H, 5-H), 6.90 (d, $J = 9$ Hz, 2H, $H_e$), 3.03 (s, 6H, N($CH_3$)$_2$), 2.55 (s, 6H, 4'-$CH_3$), 2.49 (s, 6H, 4-$CH_3$); ESMS ($CH_3OH$) $m/z$: 807 ([$M - 2ClO_4 - H$]$^+$), 404 ([$M - 2ClO_4$]$^{2+}$). Anal. calcd for $C_{45}H_{41}Cl_2N_9O_8Ru \cdot 3H_2O$: C 48.38, H 3.67, N 11.29; found C 48.16, H 3.71, N 10.94.

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

*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 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 ℃, respectively, and the quoted $m/z$ values are for the major peaks in the isotope distribution.

Cyclic voltammetric measurement was performed on an EG&G PAR 273 polarographic analyser and 270 universal programmer. The supporting electrolyte was 0.1 mol/L tetrabutylammonium perchlorate in acetonitrile freshly twice distilled 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, a platinum-wire auxiliary electrode and a saturated calomel reference electrode (SCE).

*Third-order nonlinear optical property measurement*

Acetonitrile solutions of $5.0 \times 10^{-5}$ mol/L of the ruthenium complexes were placed in a 2-mm quartz cuvette for optical measurements. Their nonlinear refraction and nonlinear absorption were measured with a linearly polarized laser light ($\lambda = 540$ nm; pulse width (FWHM) = 12 ns) generated from an excimer laser (Lambda Physics EMG 201MSC)-pumped dye laser (Lambda Physics model FL2002) system. The spatial profiles of

the optical pulses were nearly Gaussian. The laser beam was focused with a 5 cm focal-length focusing mirror. The radius of the beam waist at focus point was measured to be 30 $\mu$m (half-width at $1/e^2$ maximum). The repetition rate of laser pulse is 10 Hz. The incident and transmitted pulse energies were measured by a Laser Precision detector (RJ-7200 energy probe). The NLO properties of the samples were manifested by moving the samples along the axis of incident beam ($Z$ direction) with respect to the focal point. An aperture of 0.5 mm radius was placed in front of the detector to assist the measurement of self-defocusing effect.

## Results and discussion

### Synthesis and characterization

The mixed-ligand complexes are prepared by direct reaction of Ru(dmb)$_2$Cl$_2$ with the appropriate ligands in methanol 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 $^1$H NMR spectra. The proton chemical shifts were assigned with the aid of $^1$H-$^1$H COSY experiments and by comparison with those of similar compounds.[8,12,13,16-18] Due to the shielding influences of the adjacent L (L = IP, PIP, HOP or DMNP) and dmb, the dmb protons of the complex exhibit two distinct sets of signals. In addition, as other similar examples reported,[8,12,18] the proton resonance on the nitrogen atom of the L imidazole ring was not observed. This can be attributed to that the proton is an active proton and exchanges quickly between the two nitrogens of the imidazole ring.

### Electrochemical studies

The electrochemical data for all complexes are listed in Table 1. Each complex exhibits oxidation (one) and reduction (two or three) waves in the sweep range − 1.90 to + 1.80 V, as shown in Fig. 1 for [Ru(dmb)$_2$-(HOP)]$^{2+}$. 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 $\pi^*$ system.[19] As expected, the attachment of a phenyl ring to the IP moiety and the replacement of H atom in PIP by electron-donating groups have an effect on the Ru(II)/Ru(III) oxidation. These data are consistent with the electron donors stabilizing the Ru(III) via raising the absolute energy of the highest occupied molecular orbital (HOMO).[20-22] With reference to previous studies on similar systems,[8,12,18] the first reduction, which is usually controlled by the ligand having the most stable lowest unoccupied molecular orbital (LUMO), is assigned to a reduction centered on the 2-arylimidazo-[4,5-*f*][1,10]-phenanthroline.

**Table 1**    Electrochemical data of the ruthenium(II) complexes

| Complex | $E_{1/2}$ versus SCE$^a$ | | | |
|---------|-----------|------------------|--------|--------|
| | Ru$^{II/III}$ | Ligand reduction | | |
| 1 | + 1.19 | − 1.00 | − 1.43 | − 1.62 |
| 2 | + 1.26 | − 0.98 | − 1.42 | − 1.61 |
| 3 | + 1.23 | − 1.10 | − 1.43 | − 1.63 |
| 4 | + 1.21 | − 1.22 | − 1.45 | − 1.68 |

$^a$All complexes were measured in 0.1 mol/L NBu$_4$ClO$_4$-CH$_3$CN, error in potentials was ± 0.02 V; $T$ = (23 ± 1) ℃; scan rate = 100 mV/s.



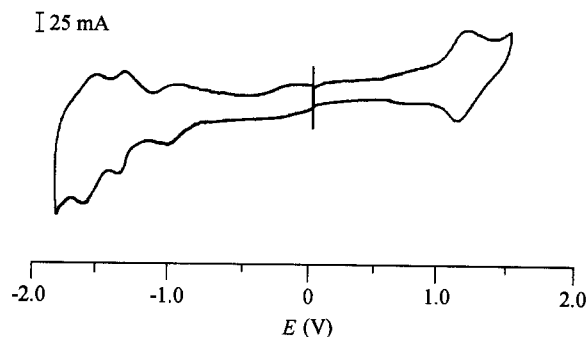**Fig. 1**    Cyclic voltammogram of [Ru(dmb)$_2$(HOP)]$^{2+}$ in CH$_3$CN.

### Optical response

The absorption spectra of the complexes were recorded in CH$_3$CN. The complexes **1—4** all show intense ligand-centered transitions in the UV region and metal-to-ligand charge transfer (MLCT) transitions in the visible region. The low-energy bands at 462, 465, 466 and 463 nm for complex **1**, **2**, **3** and **4**, respectively, are assigned as MLCT Ru (d$\pi$)→L ($\pi^*$) transitions [L = IP, PIP, HOP or DMNP]. In addition, a unique band at 345 nm

is exhibited in the absorption spectrum of complex **4**, which can be assignable to the intraligand (IL) transition of DMNP. The nonlinear optical (NLO) properties of complexes **1—4** were investigated with 540 nm laser pulses of 12 ns duration in $5.0 \times 10^{-5}$ mol/L $CH_3CN$ solutions. The nonlinear absorption components of complexes **1—4** were evaluated by $Z$-scan experiment under an open aperture configuration (Fig. 2a). The NLO absorption data obtained under the conditions used in this study can be described by Eq. (1) and (2),[23,24] which are derived to describe a third-order NLO absorptive process:

$$T(Z) = \frac{1}{q(z)\sqrt{\pi}} \int_{-\infty}^{+\infty} \ln[1 + q(Z)] \exp(-\tau^2) d\tau \tag{1}$$

$$q(Z) = \alpha_2 I_i(Z) \frac{(1 - e^{-\alpha_0 L})}{\alpha_0} \tag{2}$$

where $\alpha_0$ and $\alpha_2$ are linear and nonlinear absorptive coefficients, $L$ the thickness of the quartz cuvette for optical measurements and $\tau$ the time. Light transmittance ($T$) a function of the sample's $Z$-position (against focal point $Z = 0$).

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. 2b). The valley/peak pattern of the corrected transmittance curve so obtained shows characteristic self-defocusing behavior of propagating light in the sample. An effective third-order non-linear refractive index $n_2$ can be derived from the difference between normalized transmittance values at valley and peak positions ($\Delta T_{v-p}$) by Eq. (3), where $I$ is the incident pulsed light intensity.

$$n_2 = \frac{\lambda \alpha_0}{0.812\pi I(1 - e^{-\alpha_0 L})} \Delta T_{v-p} \tag{3}$$

In accordance with the $\alpha_2$ and $n_2$ values, the modulus of the effective third order susceptibility $\chi^{(3)}$ can be calculated by Eq. (4).[25]

$$|\chi^{(3)}| = \sqrt{\left|\frac{c\lambda n_0^2}{64\pi^3}\alpha_2\right|^2 + \left|\frac{cn_0^2}{16\pi^2}n_2\right|^2} \tag{4}$$

where $\lambda$ is the wavelength of the laser, $n_0$ the linear in-

dex of refraction of the complexes. The corresponding modulus of the hyperpolarizability $\gamma$ can be obtained from $\chi^{(3)} = \gamma \cdot NF^4$, where $N$ is the number density of the solute in the solution (in $mL^{-1}$) and $F^4 = 2.61$ is the local field correction factor. The values of $|\chi^{(3)}|$ and $|\gamma|$ are listed in Table 2.
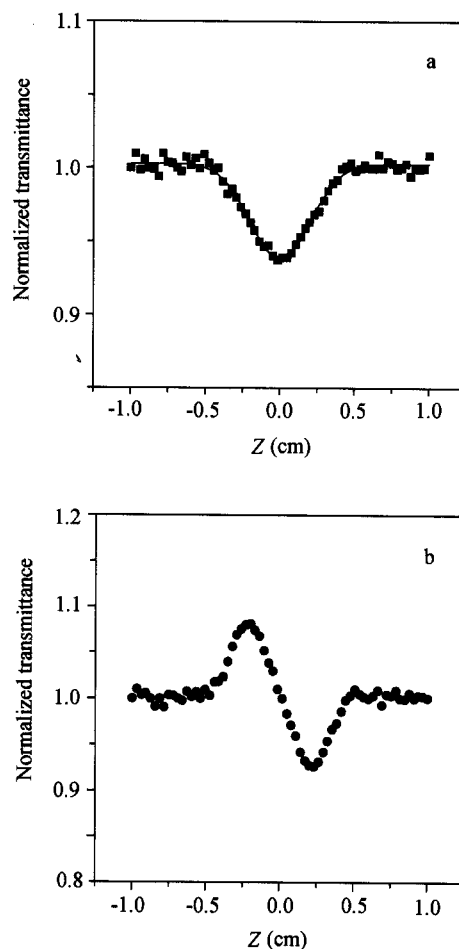


**Fig. 2**   $Z$-scan measurement of $[Ru(dmb)_2(DMNP)]^{2+}$ in $5 \times 10^{-5}$ mol/L $CH_3CN$ solution. (a) The data collected under open aperture configuration (the solid curve is a theoretical fit based on Eqs. 1 and 2); (b) the data obtained by dividing the normalized $Z$-scan data obtained under closed aperture configuration by the normalized $Z$-scan data in (a).

From the discussions above, we can reasonably state that complexes **1—4** exhibit similar NLO properties. All exhibit strong self-defocusing performances 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.[26-28] Compared with some known

**Table 2**  Measurement results of the Ru(II) complexes using *Z*-scan techniques

| Complex | $n_2$ (m$^2$/W) | $\alpha_2$ (m/W) | $\chi^{(3)}$ (esu)[a] | $\gamma$ (esu)[a] |
|---------|----------------|------------------|----------------------|-------------------|
| 1 | $-8.57 \times 10^{-18}$ | $4.81 \times 10^{-11}$ | $2.68 \times 10^{-12}$ | $3.41 \times 10^{-29}$ |
| 2 | $-1.16 \times 10^{-17}$ | $5.25 \times 10^{-11}$ | $3.60 \times 10^{-12}$ | $4.59 \times 10^{-29}$ |
| 3 | $-1.36 \times 10^{-17}$ | $8.72 \times 10^{-11}$ | $4.29 \times 10^{-12}$ | $5.47 \times 10^{-29}$ |
| 4 | $-1.43 \times 10^{-17}$ | $10.66 \times 10^{-11}$ | $4.57 \times 10^{-12}$ | $5.82 \times 10^{-29}$ |

[a] Values ± 10%.

NLO chromophores ($5.6 \times 10^{-35}$—$8.6 \times 10^{-34}$ esu for Group 10 metal alkynyl polymers at 1064 nm[29], $2.27 \times 10^{-32}$ esu for an alkynylruthenium dendrimer at 800 nm[30], $1.6 \times 10^{-28}$ esu for an half-open cubane-like [$WOS_3(CuBr)_3(\mu_2\text{-Br})$]$^{3-}$ at 532 nm[31]), the $|\gamma|$ values obtained for the new complexes are large. Due to extension of the electronic $\pi$-system, the $|\gamma|$ of complex **2** is larger than that of complex **1**. For complexes **2**, **3** and **4**, an increase in this parameter was observed on going from complex **2** to complex **4** though the difference between complex **3** and complex **4** is negligible considering the experimental errors in the data. This can be attributed to the incorporation of electron-donating groups on the ligand PIP, resulting in higher electron delocalization of the $\pi$-system and in turn enhancement of NLO effects.

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