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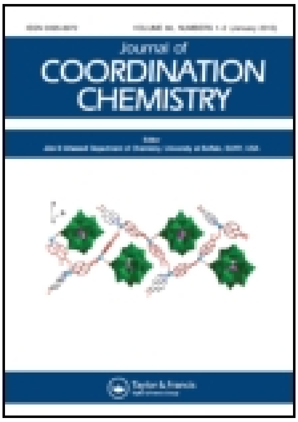

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis, characterization, and nonlinear optical responses of nickel(II) complexes with phenanthroline-based ligands

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Published online: 17 Jun 2013.

To cite this article: Zhi-Bin Cai , Li-Fen Liu , Yu-Qian Hong & Mao Zhou (2013) Synthesis, characterization, and nonlinear optical responses of nickel(II) complexes with phenanthroline-based ligands, Journal of Coordination Chemistry, 66:13, 2388-2397, DOI: 10.1080/00958972.2013.805322

To link to this article: http://dx.doi.org/10.1080/00958972.2013.805322

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Journal of Coordination Chemistry, 2013
Vol. 66, No. 13, 2388–2397, http://dx.doi.org/10.1080/00958972.2013.805322

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Synthesis, characterization, and nonlinear optical responses of nickel(II) complexes with phenanthroline-based ligands

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(*Received 8 November 2012; in final form 18 April 2013*)

Three nickel(II) complexes with phenanthroline-based ligands were synthesized and characterized by UV–visible, IR, MS, and elemental analysis. Their off-resonance third-order nonlinear optical (NLO)properties were measured using a femtosecond laser and the degenerate four-wave mixing technique. The third-order NLO susceptibilities $\chi^{(3)}$ were $3.45–4.37 \times 10^{-13}$ esu. The second-order hyperpolarizabilities γ of the molecules were $3.46–4.36 \times 10^{-31}$ esu. The response times were 50–74 fs. The influence of the molecular structure on the third-order optical nonlinearity was analyzed. The results show that highly polarizable delocalized π-conjugated electron system is the key factor leading to strong third-order optical nonlinearity.

Keywords: Nonlinear optics; DFWM technique; Nickel(II) complex; Synthesis

1. Introduction

Third-order nonlinear optical (NLO) materials have been the focus of research from both fundamental and practical points of view for the possibility of their applications in the domain of optoelectronics and photonics. A variety of materials have been investigated for third-order nonlinear optics, among which organometallic and coordination materials are especially interesting because compared with purely organic materials, they offer additional effects on the NLO responses by introducing variations on the nature, the oxidation state, and coordination sphere of the metal, as well as on the characteristics of the attached ligands [1–8].

Third-order optical nonlinearities in organic materials usually arise from the delocalized π-conjugated electron systems [9–14]. Thus, coordination to a metal of π-conjugated organic molecules may produce a significant increase in their hyperpolarizabilities γ due to the extensive electronic delocalization and polarization. 1,10-Phenanthroline (**phen**) is a classic chelating bidentate ligand for transition metal ions with a rigid, planar, hydrophobic, and electron-poor π-conjugated system. Taking advantage of these structural features, metal complexes with **phen-**based ligands have been actively studied for their catalytic, redox, photochemical, and photophysical properties [15–19]. They have very important applications to

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molecule/ion recognition and sensing [20, 21], DNA binding/cleavage [22, 23], molecular self-assembling [24, 25], etc. Recent studies also indicate that some metal complexes with **phen**-based ligands are promising candidates for NLO materials. However, the vast majority of such studies have focused on quadratic optical nonlinearities [26–30] and, to a far lesser extent, on third-order responses.

The nickel ion has an unfilled d-electron shell, which allows the possibility of low energy charge transfer transitions. Several studies show that as an excellent template, it can gather π-conjugated organic molecules to form two-dimensional (2-D) or three-dimensional (3-D) third-order NLO materials [31–38].

Based on the above consideration, in this paper, we selected **phen**, 2-(o-hydroxyphenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (**OHPIP**), and 2-(p-hydroxyphenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (**PHPIP**) as ligands for Ni(II). Three nickel(II) complexes, $[\mathrm{Ni}(\textbf{phen})_2\textbf{OHPIP}]^{2+}$ (**1**), $[\mathrm{Ni}(\textbf{OHPIP})_3]^{2+}$ (**2**), and $[\mathrm{Ni}(\textbf{PHPIP})_3]^{2+}$ (**3**), were obtained (figure 1). Their structures were characterized by UV–visible, IR, MS, and elemental analysis. By using a femtosecond laser, the off-resonance third-order optical nonlinearities of the complexes were measured with the degenerate four-wave mixing (DFWM) technique. The results show that these complexes possess large and ultrafast third-order NLO responses. The relationships between molecular structure and optical property were analyzed. This is the first report on the NLO properties of these complexes and complexes **2** and **3** are new.

2. Results and discussion

2.1. *Synthesis and characterization*

The synthetic routes to **1**–**3** are outlined in scheme 1.

Imidazole syntheses employing 1,2-diamino compounds are widely used, but in this paper, the imidazoles (**OHPIP**, **PHPIP**) were prepared from α-diketone by its reaction with aldehydes and ammonium acetate in glacial acetic acid. Ammonium acetate serves as the source of ammonia. The initial reaction is the formation of 1,10-phenanthroline-5,6-diimine, which then undergoes an aldol-type condensation with o(p)-hydroxybenzaldehyde. This is followed by 1,5-hydrogen shift and subsequent loss of water to form the desired imidazoles.

The nickel(II) complexes were synthesized by the reaction of $\mathrm{NiCl_2{\cdot}6H_2O}$ with the corresponding ligands (**phen**, **OHPIP**, and **PHPIP**), in the appropriate molar ratios, using methanol as solvent. They were isolated as perchlorates and purified by recrystallization in relatively high yield. The elemental analyses of these complexes were in agreement with their molecular formulas. The strong stretching absorption around $1110\,\mathrm{cm^{-1}}$ in FTIR spectra indicated the existence of $\mathrm{ClO_4^-}$. In the ESI-MS spectra, both signals $[\mathrm{M{-}2ClO_4}]^{2+}$ and $[\mathrm{M{-}2ClO_4{-}H}]^{+}$ were observed. Their values were consistent with the expected molecular weights. Due to their paramagnetic properties, **1**–**3** could not be characterized by ^{1}H NMR spectra.

2.2. *Absorption spectra*

UV–visible absorption spectra of **1**–**3** and the ligands (**OHPIP**, **PHPIP**) in DMF are displayed in Supplementary material. The maximum absorption peaks are at 274, 279, and 290 nm for **1**–**3**, respectively, attributed to intraligand π–π^* transitions. The band at 330 nm

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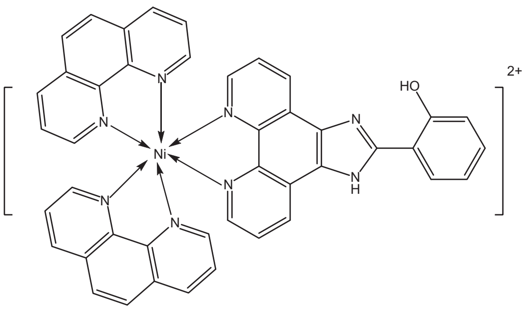

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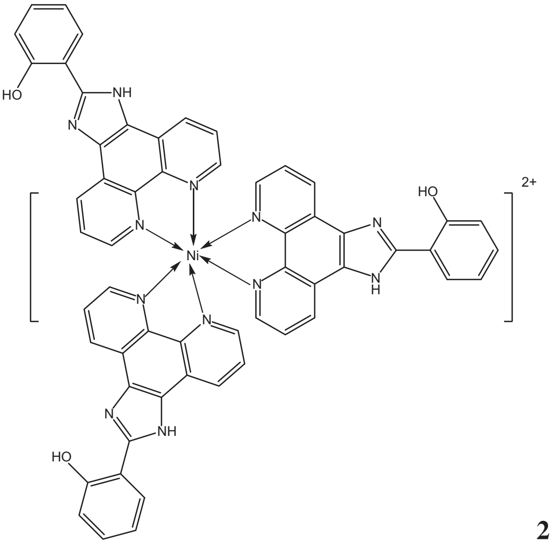

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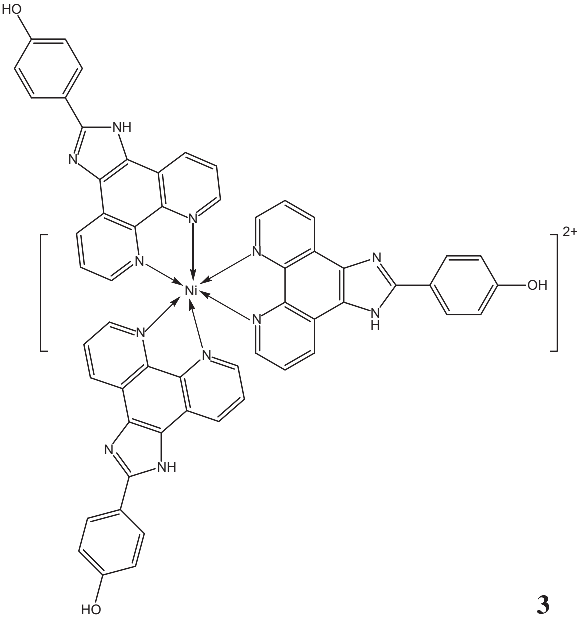

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Figure 1. Structures of the nickel(II) complexes **1**–**3**.

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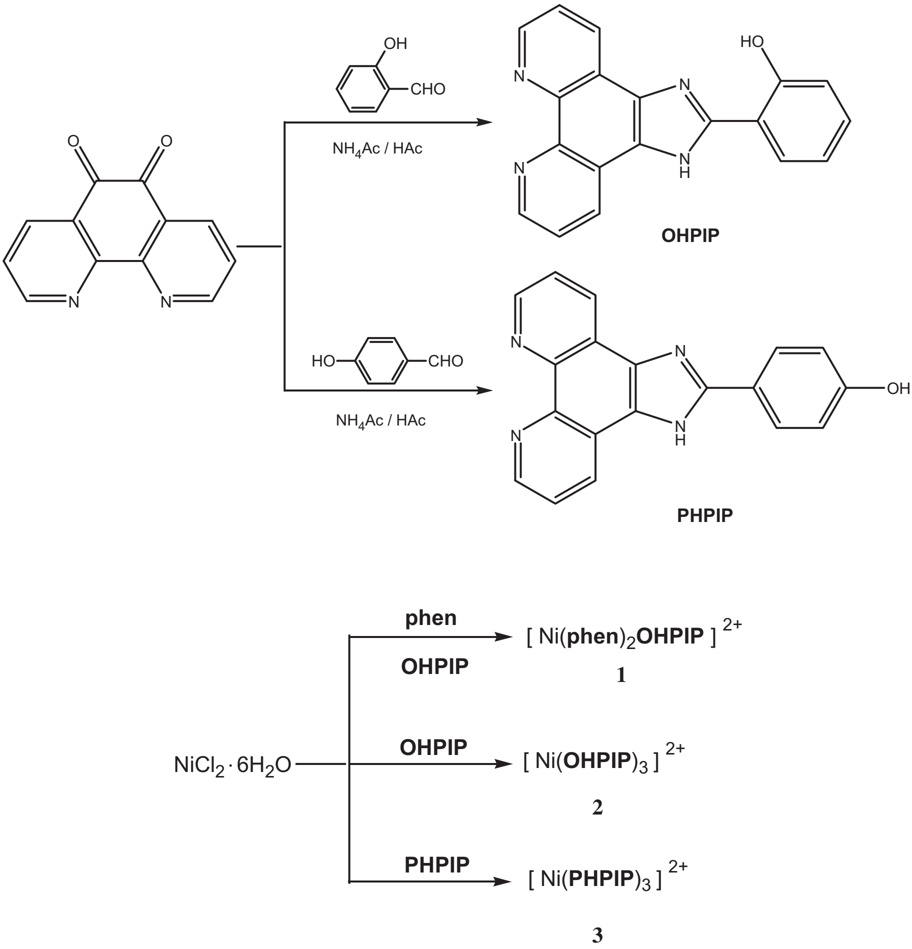

Scheme 1. Synthesis of **1**–**3**.

for **1** and **2** is related to ligand-to-ligand charge transfer (LLCT); **3** shows only a weak LLCT shoulder at 400 nm. Above 500 nm, they are essentially transparent. The laser wavelength (800 nm) used in DFWM is out of the absorption region. Thus their off-resonance third-order optical nonlinearities can be measured. A good nonlinearity–transparency tradeoff which is very important for practical applications of NLO materials is obtained.

2.3. *Third-order NLO properties*

The third-order NLO susceptibility $\chi^{(3)}$ is measured via comparison with that of a reference sample CS_2, calculated from the DFWM signal (I), the linear refractive index (n), the sample thickness (L), and absorption correction factor using the following equation [39]:

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$$\chi_{\mathrm{s}}^{(3)} = \left(\frac{I_{\mathrm{s}}}{I_{\mathrm{r}}}\right)^{1/2}\frac{L_{\mathrm{r}}}{L_{\mathrm{s}}}\left(\frac{n_{\mathrm{s}}}{n_{\mathrm{r}}}\right)^{2}\frac{\alpha L\exp(\alpha L/2)}{1-\exp(-\alpha L)}\,\chi_{\mathrm{r}}^{(3)} \tag{1}$$

where the subscripts "s" and "r" represent the parameters for the sample and CS_2, and α indicates the linear absorption coefficient. The fraction $\frac{\alpha L\exp(\alpha L/2)}{1-\exp(-\alpha L)}$ comes from the sample absorption and equals approximately 1, while the sample has little absorption around the employed laser wavelength. The values of $\chi_{\mathrm{r}}^{(3)}$ and n_{r} for CS_2 are 6.7×10^{-14} esu and 1.632, respectively [40].

The second-order hyperpolarizability γ of a molecule in isotropic media is related to the solution $\chi^{(3)}$ by [41]:

$$\gamma = \chi^{(3)}/Nf^4 \tag{2}$$

where N is the number density of the solute per milliliter, related to the molar concentration c by $N = N_{\mathrm{A}}c$ with N_{A} being Avogadro's number; f^4 is the local field correction factor which is $[(n^2+2)/3]^4$ (n is the linear refractive index of solution, measured by 2WAJ Abbe refractometer).

The dependence of DFWM signal intensity on the delay time of the input beam is shown in figure 2. The curves are obtained via fitting the time convolution between autocorrelation function of pulse and single exponent decline function $\exp\left(\frac{t}{-T_2}\right)$. The fitting expressions are shown in equation (3) and equation (4). The response times of the samples can be obtained from figure 2.

$$I(t) = \exp\left(-\frac{4\ln 2t^2}{T^2}\right) \tag{3}$$

$$S(\tau) = \int \exp\left(-\frac{t}{T_2}\right)dt \int I(t-t')I(t)dt' \tag{4}$$

The values of $\chi^{(3)}$, γ, and response times for the samples are deduced and calculated from the experimental results which are listed in table 1. From table 1 and it is found that **1**–**3** show large second-order molecular hyperpolarizabilities γ, on the order of 10^{-31} esu, which are comparable with those of some known NLO organometallic and coordination materials [42–47].

For **1**, Ni(II) is six-coordinate octahedral, ligated by six nitrogens from two **phen** and one **OHPIP**. **OHPIP** consists of imidazole-fused **phen** and o-hydroxyphenyl radical in the 2-position. **Phen** possesses a planar and rigid π-conjugated electron system, which can be polarized in the light induction and exhibits a relatively large γ of 1.76×10^{-31} esu [48]. The γ value of **1** is approximately twice that of **phen**, mainly due to the incorporation of Ni(II) with an open d-shell involving low energy charge transfer transitions. The d orbitals interact strongly with π-electron orbitals of the ligands, resulting in a larger polarizable system and better NLO responses.

Compared with **1**, **2** and **3** feature extended π-conjugated ligands containing three 2-(hydroxyphenyl)imidazole-fused **phen** units rather than one. The electron-donating hydroxy on the benzene ring can effectively push electrons onto the ring system. Such

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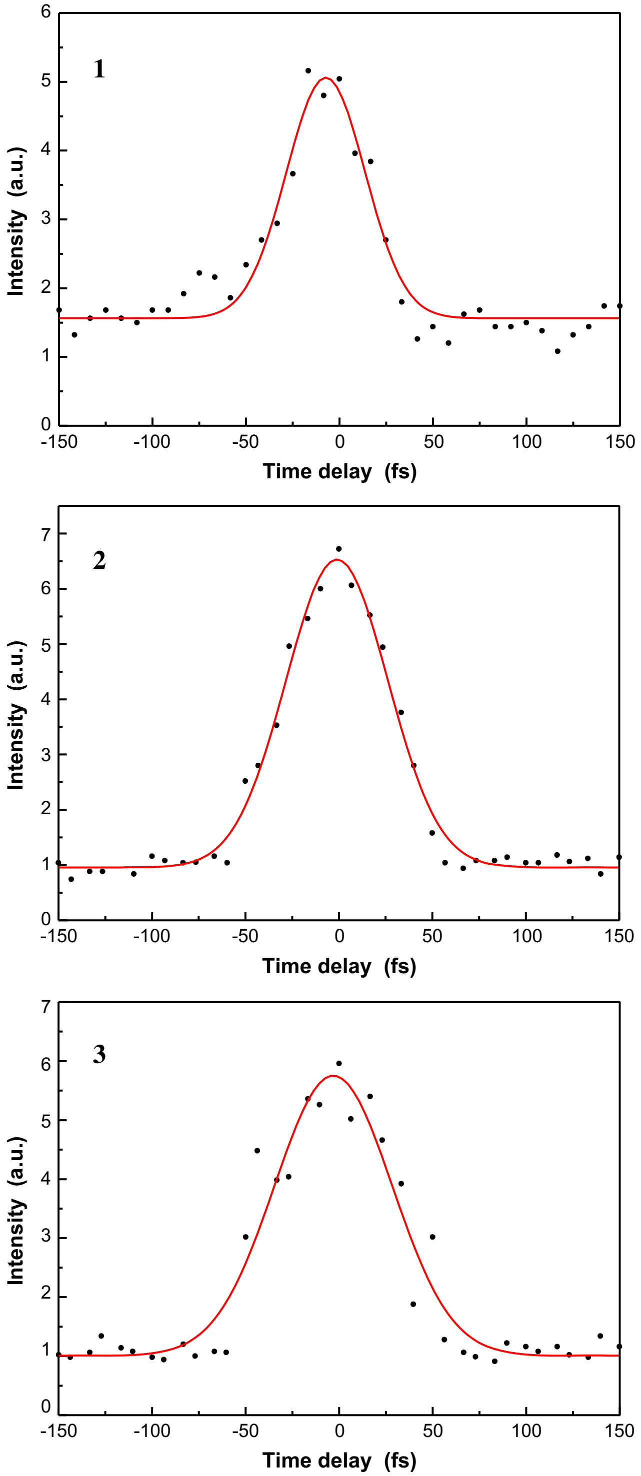

Figure 2. DFWM signal *vs.* delay time for **1**–**3** in DMF solution.

Table 1. The values of $\chi^{(3)}$, γ, and response times for **1**–**3**.

Sample	n	$\chi^{(3)}$ (10^{-13} esu)	γ (10^{-31} esu)	Response time (fs)
1	1.4308	3.45	3.46	50
2	1.4326	4.37	4.36	64
3	1.4325	4.03	4.02	74

extended π-conjugated ligands with acceptor and donor, strengthen intramolecular charge transfer, and hence lead to higher γ values.

Comparison of γ value for **2** with that for **3** indicates that the position of hydroxy affects the NLO responses. For **OHPIP**, the benzene ring is almost coplanar with the imidazole ring owing to the formation of an intramolecular hydrogen bond between the ortho hydroxy and nitrogen of the imidazole ring. The extended coplanarity facilitates electronic communication and charge transfer transitions, so the γ value of **2** with **OHPIP** is larger than that of **3** with **PHPIP**.

Normally, the time domain response of the sample should contain several processes of different time scales. The third-order NLO response time induced by delocalized electrons is believed to be 10^{-14}–10^{-15} s. The response time induced by molecular reorientation is 10^{-11}–10^{-12} s, that induced by electrostriction is 10^{-8}–10^{-9} s and that induced by heat absorption is 10^{-1}–10^{-7} s. From figure 2, we obtain the response times of **1**–**3** to be 50–74 fs, which is commonly accepted to be the contribution from transient motion of the π-conjugated electron distribution.

3. Conclusions

Three nickel(II) complexes with **phen**-based ligands were synthesized and characterized by UV–visible, IR, MS, and elemental analysis. Their off-resonance third-order NLO properties were investigated by DFWM with the laser duration of 80 fs at 800 nm. The large and ultrafast NLO responses for these complexes are due to highly polarizable electronic networks in their delocalized π-conjugated systems. In addition, they are also transparent and stable, thereby making them promising candidates for NLO materials.

4. Experimental

4.1. *Materials*

1,10-Phenanthroline-5,6-dione was prepared according to the literature method [49]. Other materials were commercially available and of reagent grade. All of them were used without purification.

4.2. *Physical measurements*

FTIR spectra were recorded on a Vector 22 spectrometer using KBr pellets. ^{1}H NMR spectra were collected on an AVANCE III 500 MHz apparatus, with TMS as internal standard

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and DMSO-d_6 as solvent. UV–visible spectra were recorded on a Shimadzu UV-2550 UV–visible spectrometer. Elemental analyses were conducted on a Thermo Finnigan Flash EA 1112 apparatus. Mass spectra were taken on a Therm LCQ TM Deca XP plus ion trap mass spectrometer instrument. Melting points were measured on an X-4 micromelting point apparatus without correction.

4.3. *Synthesis*

4.3.1. 2-(o-Hydroxyphenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (OHPIP). A mixture of 1,10-phenanthroline-5,6-dione (1.05 g, 5 mmol), o-hydroxybenzaldehyde (0.73 g, 6 mmol), ammonium acetate (7.7 g, 100 mmol), and glacial acetic acid (16 mL) was heated under reflux with stirring for 3 h. The cooled solution was diluted with H_2O and neutralized with concentrated aqueous ammonia. The precipitate was collected and recrystallized from DMF to give yellow granular crystals. Yield: 1.3 g, 83.3%. m.p. > 300 °C. ^{1}H NMR (500 MHz, DMSO-d_6), δ (ppm): 13.98 (s, 1H), 12.75 (s, 1H), 9.09 (dd, 2H, $J_1 = 4.4$ Hz, $J_2 = 1.5$ Hz), 8.98 (dd, 2H, $J_1 = 7.8$ Hz, $J_2 = 1.5$ Hz), 8.21–8.23 (m, 1H), 7.89 (dd, 2H, $J_1 = 7.8$ Hz, $J_2 = 4.4$ Hz), 7.41–7.45 (m, 1H), 7.11–7.14 (m, 2H).

4.3.2. 2-(p-Hydroxyphenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (PHPIP). This ligand was synthesized as above using p-hydroxybenzaldehyde. The product was yellow needle crystals. Yield: 1.35 g, 86.5%. m.p. > 300 °C (Lit. m.p. > 300 °C [50]). ^{1}H NMR (500 MHz, DMSO-d_6), δ (ppm): 13.52 (s, 1H), 9.98 (s, 1H), 9.03 (dd, 2H, $J_1 = 4.4$ Hz, $J_2 = 1.5$ Hz), 8.91 (dd, 2H, $J_1 = 8.8$ Hz, $J_2 = 1.5$ Hz), 8.12 (d, 2H, J = 7.8 Hz), 7.83 (dd, 2H, $J_1 = 8.8$ Hz, $J_2 = 4.4$ Hz), 6.99 (d, 2H, J = 7.8 Hz).

4.3.3. [2-(1H-Imidazo[4,5-f][1,10]phenanthrolin-2-yl-κN7,κN8)phenol]bis(1,10-phenanthroline-κN1,κN10)-nickel(2+) (1). A mixture of nickel dichloride hexahydrate (0.24 g, 1 mmol), **phen** (0.4 g, 2.2 mmol), and methanol (20 mL) was heated under reflux with stirring for 2 h. A solution of **OHPIP** (0.37 g, 1.2 mmol) in methanol (15 mL) was then added and further stirred under reflux for 3 h. The reaction mixture was cooled to room temperature and a saturated aqueous sodium perchlorate solution was added. The precipitate was collected and recrystallized from DMF twice to give a light yellow crystalline powder. Yield: 0.67 g, 70.6%. FTIR (KBr), v (cm^{-1}): 3431 (v_{NH}, v_{OH}), 3071 ($v_{=CH}$), 1626, 1515, 1485, 1409, 1102 (v_{ClO4}), 813 ($\delta_{=CH}$), 729 ($\delta_{=CH}$), 623 (δ_{ClO4}). ESI-MS (CH_3CN): *m/z* 728.9 ($[M–2ClO_4–H]^+$), 365.3 ($[M–2ClO_4]^{2+}$). Anal. Calc. for $C_{43}H_{28}Cl_2N_8NiO_9 \cdot H_2O$: C, 54.46; H, 3.19; N, 11.82. Found: C, 54.46; H, 3.58; N, 12.09%.

4.3.4. Tris[2-(1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl-κN7,κN8)phenol]-nickel(2+) (2). A mixture of nickel dichloride hexahydrate (0.24 g, 1 mmol), **OHPIP** (1.03 g, 3.3 mmol), and methanol (30 mL) was heated under reflux with stirring for 3 h. The reaction mixture was cooled to room temperature and a saturated aqueous sodium perchlorate solution was added. The precipitate was collected and recrystallized from DMF twice to give a yellow crystalline powder. Yield: 0.78 g, 63.9%. FTIR (KBr), v (cm^{-1}): 3435 (v_{NH}, v_{OH}), 3076 ($v_{=CH}$), 1627, 1514, 1485, 1409, 1120 (v_{ClO4}), 812 ($\delta_{=CH}$), 734 ($\delta_{=CH}$), 623 (δ_{ClO4}). ESI-MS (CH_3CN): *m/z* 993.5 ($[M–2ClO_4–H]^+$), 498.0 ($[M–2ClO_4]^{2+}$). Anal. Calc.

for $C_{57}H_{36}Cl_2N_{12}NiO_{11}\cdot 1.5H_2O$: C, 56.04; H, 3.22; N, 13.76. Found: C, 56.03; H, 3.43; N, 13.48%.

4.3.5. Tris[4-(1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl-κN7,κN8)phenol]-nickel(2+) (3). This complex was synthesized using a procedure similar to that described for **2**, with **PHPIP** instead of **OHPIP**. The product was a yellow crystalline powder. Yield: 0.77 g, 61.7%. FTIR (KBr), ν (cm^{-1}): 3404 (ν_{NH}, ν_{OH}), 3080 ($\nu_{=CH}$), 1611, 1508, 1483, 1452, 1116 (ν_{ClO4}), 813 ($\delta_{=CH}$), 734 ($\delta_{=CH}$), 624 (δ_{ClO4}). ESI-MS (CH_3CN): *m/z* 993.2 ($[M–2ClO_4–H]^+$), 497.3 ($[M–2ClO_4]^{2+}$). Anal. Calc. for $C_{57}H_{36}Cl_2N_{12}NiO_{11}\cdot 3H_2O$: C, 54.83; H, 3.39; N, 13.46. Found: C, 54.92; H, 3.04; N, 13.23%.

4.4. *Nonlinear optical measurements*

The third-order NLO properties were measured using femtosecond DFWM technique, with a Ti: Sapphire laser. The pulse width was determined to be 80 fs on a SSA25 autocorrelator. The operating wavelength was centered at 800 nm. The repetition rate of the pulses was 1 kHz. During the measurement, the laser was very stable (rms < 0.1%). The input beam was split into two beams k_1 and k_2 with nearly equal energy by using a beam splitter, then focused on the sample. The beam k_2 passed through a delay line driven by a stepping motor in order that the optical path length difference between the k_2 and k_1 beams could be adjusted during the measurement. The angle between the beams k_1 and k_2 was about 5°. When k_1 and k_2 were overlapped spatially in the sample, the generated signal beam k_3 or k_4 passed through an aperture, recorded by a photodiode and then analyzed by a Lock-in amplifier and computer.

The experiments were performed at 22 °C. The samples dissolved in DMF at $5 \times 10^{-4}\,mol\,L^{-1}$ were placed in a 1 mm thick quartz cell. The solvent DMF has no nonlinear signal under the light intensity adopted. So the third-order optical nonlinearities measured come from the complexes themselves.

Acknowledgment

We are grateful to the National Natural Science Foundation of China for financial support (Grant No. 21103151).

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