Optics Communications 283 (2010) 2228–2233

Contents lists available at ScienceDirect

Optics Communications

journal homepage: www.elsevier.com/locate/optcom

Synthesis and third-order optical nonlinearities of nickel complexes of 8-hydroxyquinoline derivatives

Yan Qian [a,b,*], Minmin Cai [a], Shuangqing Wang [b], Yuanping Yi [b], Zhigang Shuai [b], Guoqiang Yang [b,*]

[a] Jiangsu Key Lab for Organic Electronics and Information Displays and Institute of Advanced Materials (IAM), Nanjing University of Posts and Telecommunications (NUPT), 9 Wenyuan Road, Nanjing 210046, China
[b] Beijing National Laboratory for Molecular Sciences, Key Laboratory of Photochemistry and Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

ARTICLE INFO

Article history:
Received 1 September 2009
Received in revised form 11 January 2010
Accepted 11 January 2010

Keywords:
Third-order nonlinearity
Z-scan technique
Self-defocusing
Two-photon absorption
Nickel complex of 8-hydroxyquinoline

ABSTRACT

A nickel complex of 5-(acrylamido)methyl-8-hydroxyquinoline, bis-(5-(acrylamido)methyl-8-hydroxyquinolino) nickel(II) (Ni(AAMQ)$_2$) has been synthesized and its third-order nonlinear optical properties was investigated with respect to that of bis-(8-hydroxyquinolino) nickel(II) (NiQ$_2$) by single beam Z-scan technique. The real parts (γ_R) of the molecular second-order hyperpolarizabilities were -6.0×10^{-46} and -5.5×10^{-46} m^5/v^2 for NiQ$_2$ and Ni(AAMQ)$_2$, respectively, indicative of similar nonlinear refraction both in sign and in magnitude. After substitution of an acrylamidomethyl group to the 8-hydroxyquinoline (8-HQ) ligand, the nonlinear absorption coefficient of Ni(AAMQ)$_2$ was enhanced by more than two times. The corresponding imaginary part (γ_I) of the molecular second-order hyperpolarizability was 3.4×10^{-46} m^5/v^2 for Ni(AAMQ)$_2$ while 1.6×10^{-46} m^5/v^2 for NiQ$_2$. The increase in nonlinear absorption was attributed to the substitution effect and the enhanced transition dipole moment due to the participation of δ-donor group of CH$_2$ in the molecular conjugation.

1. Introduction

In the past two decades, the third-order nonlinear optical (NLO) properties have triggered large scale of theoretical and experimental investigations in many research groups [1–6]. In particular, organometallic complexes have attracted significant interests due to their highly improved nonlinearity caused by intense charge transfer between the metal and the ligands, and by the reversibly switched nonlinearity relating to the multiple electronic states of the metal atoms. Complexes of π-excessive heterocyclic aromatic compounds have always been the subjects of scientific concerns in this field [4–6].

Moreover, two-photon absorption (TPA) has attracted increasing attentions in relation to various applications involving optical data storage, high-resolution 3-dimensional (3D) imaging of biological systems, laser up-conversion, photodynamic therapy, 3D microfabrication, and optical power limiting [7–11]. Numerous attempts were made to enhance the TPA response by increasing the electron-accepting ability, exploring the dendrimer systems and increasing the transition dipole moments [12–14].

In the work of Barder et al. the first order and second-order polarizabilities of some simple hydroxyquinoline derivatives were calculated by the coupled perturbed Hartree–Fork (CPHF) method [2,3], and a tungsten dioxo complex of 8-hydroxyquinoline (8-HQ) was investigated for its third-order optical properties [15]. In our previous work, some phthalocyanines showed significant nonlinear optical properties and the structure–property relationships of these molecules were studied [16,17]. In this work, a nickel complex of 5-substituted 8-hydroxyquinoline, bis-(5-(acrylamido)methyl-8-hydroxyquinolino) nickel(II) (Ni(AAMQ)$_2$) has been synthesized and its third-order nonlinear optical properties was investigated with respect to that of bis-(8-hydroxyquinolino) nickel(II) (NiQ$_2$) by single beam Z-scan technique with a 7 ns, 1064 nm Nd: YAG laser system. Both NiQ$_2$ and Ni(AAMQ)$_2$ possessed strong self-defocusing nonlinearities, comparable to those reported third-order nonlinear optical refraction data [18–21]. What's more important, with the acrylamidomethyl group substituted at 5-position of the ligand of 8-HQ, Ni(AAMQ)$_2$ exhibited a highly two-photon absorption as compared with NiQ$_2$, due to substitution effect for enhancement of the dipole moment caused by participation of δ-donor group of CH$_2$ in the molecular conjugation.

---

* Corresponding authors. Address: Jiangsu Key Lab for Organic Electronics and Information Displays and Institute of Advanced Materials (IAM), Nanjing University of Posts and Telecommunications (NUPT), 9 Wenyuan Road, Nanjing 210046, China. Tel.: +86 25 85866396; fax: +86 10 85866396 (Y. Qian), tel.: +86 10 82617263; fax: +86 10 82617315 (G. Yang).
E-mail addresses: qianyan@iccas.ac.cn, iiamyqian@njupt.edu.cn (Y. Qian), gqyang@iccas.ac.cn (G. Yang).

0030-4018/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.optcom.2010.01.026

2. Experimental

2.1. Synthesis

2.1.1. Materials

N-Hydroxymethyl acrylamide (98%) was purchased from TCI and 8-hydroxyquinoline (99%) was purchased from Beijing Chemical Reagents. Both the chemicals were used directly without further purification.

2.1.2. Synthesis of 5-(acrylamido)methyl-8-hydroxyquinoline(AAMQ) [22]

8-Hydroxyquinoline (0.785 g, 5.41 mmol) was dissolved in 2 ml 98% H_2SO_4, stirred with nitrogen inlet and protected from moisture. *N*-Hydroxymethyl acrylamide (0.552 g, 5.47 mmol) was added in small portions. After reaction for 2 days, the solution was poured over crushed ices and then neutralized with NaOH and $NaHCO_3$. The white precipitate formed was filtered and washed with quantity of water, then dried in vacuum overnight to give 1.04 g crude products (85%). After re-crystallization from ethanol for three times, the pure white needle-like solid (0.37 g, 31%) was obtained.

2.1.3. Synthesis of NiQ_2 and $Ni(AAMQ)_2$ [23]

Ni $(CH_3COO)_2 \cdot 4H_2O$ (0.172 g, 0.69 mmol) solution in ethanol was slowly added into a ethanol solution of AAMQ (0.20 g, 1.38 mmol) and triethyl amine (NEt_3) 0.067 g, 0.66 mmol). A yellow green precipitate was quickly formed. After reaction for 24 h, the precipitate was filtrated and washed with ethanol several times, then dried in vacuum. Purification was achieved by repeatedly adding slowly the condense dimethyl sulfoxide (DMSO) solution of the nickel complex into plenty of water with continuously shaking to precipitate. NiQ_2 was synthesized according to the previously reported method [24].

2.2. NLO measurements

The third-order nonlinear optical response of the complexes was probed by the single beam Z-scan technique [1]. A DMSO solution of each sample was placed in a 1-mm glass cuvette for NLO measurements. Using a single beam in a focused geometry, the transmittances of a nonlinear medium, as a function of the sample position z, were related to the nonlinear refraction and nonlinear absorption for the closed and open-aperture geometries, respectively. Thus, with the sample moving along the laser pulse propagation direction, the nonlinear refraction and nonlinear absorption index could be obtained by recording the incident and transmitted pulse energies. The laser source was a Q-switched Nd: YAG laser operating at 1064 nm with a pulse width of 7 ns (FWHM) and a repetition rate of 10 Hz. The spatial distribution of the pulse was nearly Gaussian after passing through a spatial filter. The pulse was divided into two parts by a beam filter; the reflected part was taken as the reference representing the incident pulse energy and the transmitted beam was focused through the sample. The incident and the transmitted pulse energies were measured simultaneously by two detectors, respectively.

2.3. Calculation method

The geometries of the two molecules were first optimized using density functional theory (DFT) at B3LYP/6-31G(d) level and then the excited-state information was obtained by time-dependent density functional theory (TDDFT) at the same level. All calculations are performed with GAUSSIAN03 package [25].

3. Results and discussion

3.1. Synthesis

The substituted 5-(acrylamido)methyl-8-hydroxyquinoline was synthesized according to Scheme 1, by a specific Friedel–Crafts reaction of 8-HQ with *N*-hydroxymethyl acrylamide at 0 °C with modification of the previous synthetic route [26]. Details of the synthesis were described in the experimental section. The substitution of the 2-position of 8-HQ was effectively avoided by reacting at a lower temperature (0 °C) with a longer reaction time (2 days), ensuring a relatively high yield of 5-mono-substituted product. Complete purification was accomplished by re-crystallization from

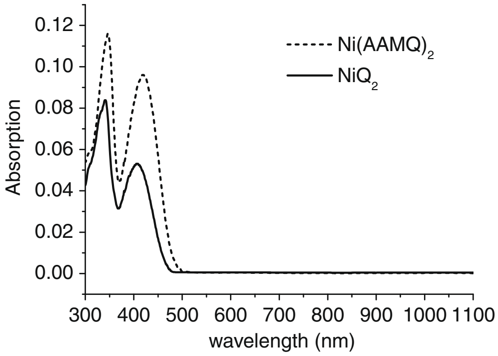
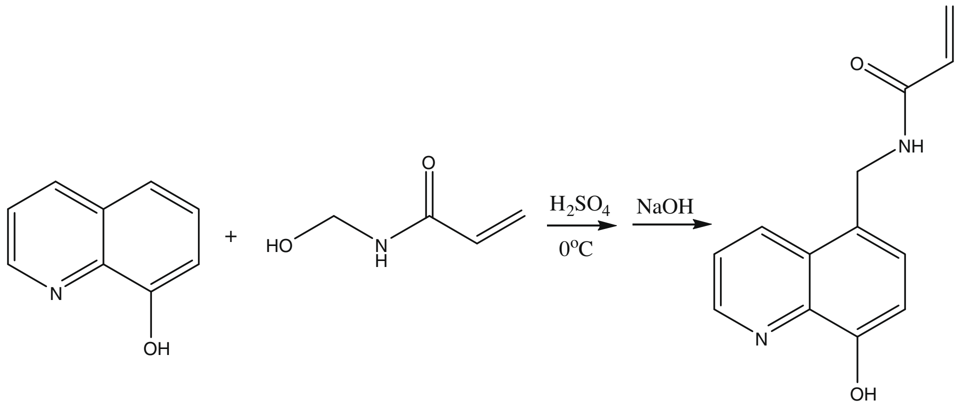


Fig. 1. UV–vis spectra of 2×10^{-5} M NiQ_2 (solid) and $Ni(AAMQ)_2$ (dash) complexes in DMSO solution.



Scheme 1. The synthesis of 5-(acrylamido)methyl-8-hydroxyquinoline (AAMQ).

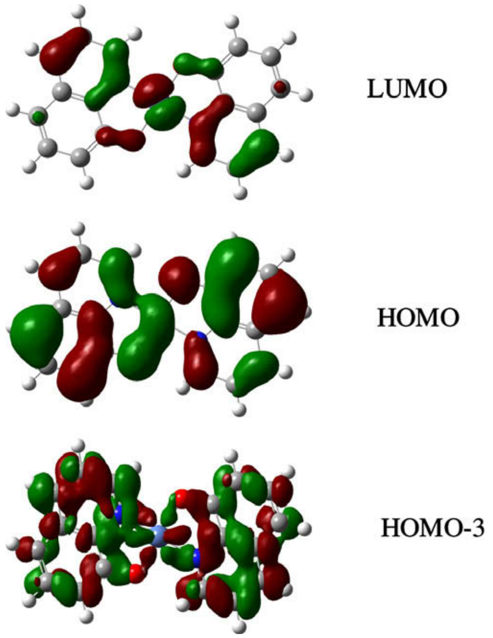


Fig. 2. The frontier molecular orbitals of NiQ_2.

hot ethanol. The corresponding nickel complexes $Ni(AAMQ)_2$ was synthesized as NiQ_2 [24].

3.2. UV–vis spectra

Electronic absorption spectrum of the Ni(II) complexes of 8-HQ derivatives showed their linear absorptions in DMSO (Fig. 1) and there was almost no absorption at 1064 nm. The UV–vis spectrum profiles of NiQ_2 and $Ni(AAMQ)_2$ were generally similar, with a slight red shift for $Ni(AAMQ)_2$. They presented two intense bands (ε higher than 1000 $mol^{-1}\,dm^3\,cm^{-1}$) occurring at $\lambda < 500$ nm – one absorption band of 315–370 nm and another band of 370–500 nm. By analyzing the related frontier molecular orbitals (Figs. 2 and 3), the absorption at the short wavelength region was caused by intra-ligand transitions; another band at longer wavelength region of 370–500 nm was ascribed to a π–π^* star ligand transition, where charge density is transferred from oxygen to nitrogen, consistent with the previously published results [27] In our work, both compounds of NiQ_2 and $Ni(AAMQ)_2$ preferred a square–planar dsp^2 covalent structure, showing a characteristic absorption band near 400 nm which is lacking in the Ni chelates of sp^3 ionic structure [28,29]. The maximum absorption wavelengths (λ_{max}) and corresponding absorption coefficients (ε) of the absorption bands were summarized in Table 1.

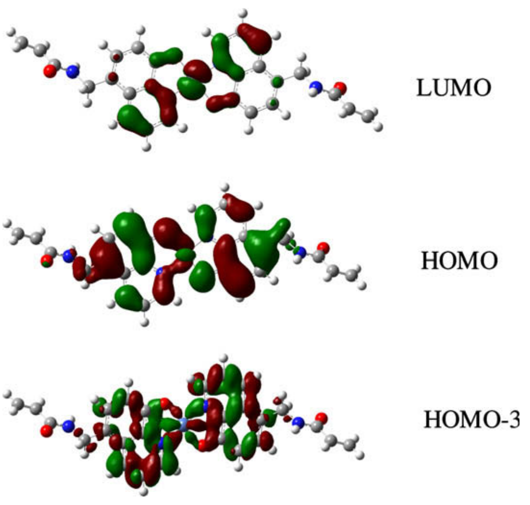


Fig. 3. The frontier molecular orbitals of $Ni(AAMQ)_2$.

Table 1
The calculated maximum wavelength, type of transition and oscillator strengths for DHIA and DHBIA compared with the experimental absorption.

Compound	Calculated absorption		Experimental absorption		
	λ_{cal} (nm)	Orbital transition	f	λ_{exp} (nm)	ε ($mol^{-1}\,dm^3\,cm^{-1}$)
NiQ_2	520	HOMO → LUMO	0.10	407	2654
	371	HOMO−3 → LUMO	0.15	341	4200
$Ni(AAMQ)_2$	519	HOMO → LUMO	0.151	419	4800
	372	HOMO−3 → LUMO	0.20	346	5800

3.2.1. NLO refraction

The NLO responses of the two complexes were measured using thin-sample analysis functions derived by Sheik-Bahae et al. [1]. The results in the closed-aperture experiments as shown in Fig. 4, the peak-valley shape indicated a negative nonlinear refraction for the samples and both the compounds possessed strong self-defocusing properties. In this case, the thin nonlinear samples acted as an intensity dependent lens. As it was scanned along the beam axis, their effective focal length would change with the incident intensity. This kind of change would be reflected in the intensity distribution at the aperture in the far field. The extent of energy transmitted by the aperture depended not only on the sample location along the z-axis but also on the sign of n_2. For $z < 0$, the lensing effect caused the beam to come later to the focus so that the aperture transmittance increased, as illustrated in Fig. 4. Near $z = o$, the thin lens had little effect on a focus beam and the aperture transmittance returned to its low intensity value. For $z > 0$, the negative lensing caused the beam divergence to increase, resulting in a decreased aperture transmittance.When the intensity of the signal was dependent on the cubic power of the incident laser beam, the third-order susceptibilities of the sample could be determined by using CS_2 as a reference under identical conditions [30–33]. The nonlinear refractive index of CS_2 (n_{2,CS_2}) was considered as $(3.1 \pm 0.2) \times 10^{-18}$ m^2/W. This value was valid for either picosecond timescale or nanosecond timescale, relatively independent of wavelength over the visible and near infrared region [32].The nonlinear refraction indexes n_2 of NiQ_2 and $Ni(AAMQ)_2$, were estimated to be -3.9×10^{-18} and -3.2×10^{-18} m^2/W, respectively. The corresponding real parts of molecular second-order hyperpolarizabilities γ_R were -6.0×10^{-46} and -5.5×10^{-46} m^5/W for NiQ_2 and $Ni(AAMQ)_2$, respectively. In Table 2 the nonlinear parameters correlated to refraction were summarized and they were comparable to those reported data of other nickel complexes [18–21].

3.2.2. NLO absorption

The open-aperture Z-scan signals (Fig. 5) obviously showed that NiQ_2 and $Ni(AAMQ)_2$ exhibited nonlinear absorption. There was a dip in the signal around the sample position of $z = 0$ mm, indicative of reduced transmission of 1064 nm pulses at the focus, caused by a positive nonlinear absorption. The transmittance of a material would significantly change when the intensity of fluence was sufficiently high, owing to the greatly enhanced probability of absorbing more than one photon.With the sample shifted along the axis, the actual incident pulse energy intensity on the irradiated area of

Table 2
Nonlinear refraction properties of nickel complexes of 8-HQ derivatives at 1064 nm.

Materials	n_2 10^{-18} m^2/W	n_2 10^{-11} esu	$\chi_R^{(3)}$ 10^{-20} m^2/v^2	$\chi_R^{(3)}$ 10^{-11} esu	γ_R 10^{-46} m^5/v^2	γ_R 10^{-32} esu	References
NiQ_2[a]	−3.9	−1.3	−2.8	−1.8	−6.0	−4.3	This work
$Ni(AAMQ)_2$[a]	−3.2	−1.1	−2.5	−1.7	−5.5	−3.9	This work
$Ni(DMG)_2$[b]	–	1.2	–	–	–	–	Ref. [18]
$Ni(CtCR)(PPh_3)(\eta\text{-}C_5H_5)$	–	–	–	–	–	$-1.5–64 \times 10^{-3}$	Ref. [19]
$Ni(DA\text{-}salen)_2$[c]	$8.5–21 \times 10^{-3}$	–	$8.1–20 \times 10^{-3}$	–	–	–	Ref. [20]
$Ni_2(X\text{–}N{=}CHC_6H_4\text{-}o\text{-}O]_2$[d]	$-3.7–6.9 \times 10^{-1}$	–	–	$-2.5–4.6 \times 10^{-2}$	–		Ref. [21]

Concentrations of samples/incident wavelength: a: 2×10^{-2} M/1064 nm, b: thin film/580 nm, c: 1.0×10^{-3} M/1064 nm, d: 3.9×10^{-2} M/532 nm.

the sample varied at different positions; it was amplified near the focus ($z = 0$) and was weak in the far field. The incident energy of the focusing light at different positions I_z was:

$$I_z = I_0 \frac{S_z}{S_0} = I_0 \frac{\pi(\frac{\omega_0}{2})^2}{\pi(\frac{r_z}{2})^2} = I_0 \frac{\omega_0^2}{r_z^2} \tag{1}$$

S_0 and S_z were the incident light areas at focus and at z position, respectively.The minimum beam waist of the focused laser ω_0 was determined to be 25.66 μm and the radius of the incident light was 0.5 mm. So the radius of the focusing light at z position was $r_z = \frac{|z|+8.4}{8.4}\omega_0$.

Then,

$$I_z = I_0 \times \left(\frac{8.4}{|z| + 8.4}\right)^2 \tag{2}$$

The absorbed pulse energy at z position was

$$A_z = (1 - T_z)I_0 \tag{3}$$

The plots of Log (absorbed pulse energy) versus Log (the incident pulse energy after focusing) ($\text{Log}\,A_z - \text{Log}\,I_z$) for these two compounds were shown in Fig. 6. For NiQ_2, the slopes of the curve of $\text{Log}\,A_z$ versus $\text{Log}\,I_z$ was about 2.09 in the range of $|z| = 10–20$ mm, where the signal of transmittance was changed continuously with changing z positions. For $Ni(AAMQ)_2$, the slope was 1.94 in the range of $|z| = 15–25$ mm. In both cases the nonlinear absorption could be considered as proportional to the square of the instantaneous intensity ($dI/dz = -\alpha I - \beta I^2$, where α was the linear absorption coefficient and β was the nonlinear absorption coefficient). Therefore the mechanism of the nonlinear absorption could be mainly attributed to the two-photo absorption (TPA) of the incident light.

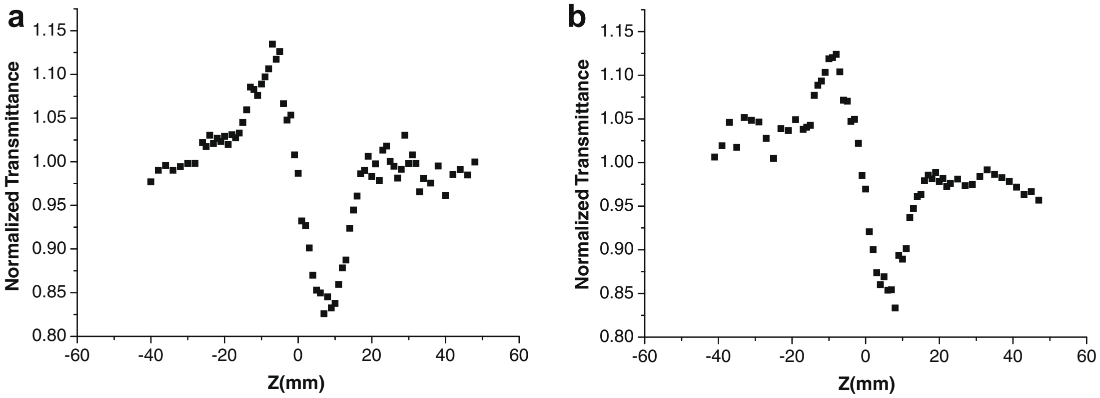


Fig. 4. Normalized transmittance data of closed-aperture Z-scan for the complexes of NiQ_2 (a) and $Ni(AAMQ)_2$, (b) in DMSO solution (2×10^{-2} M).

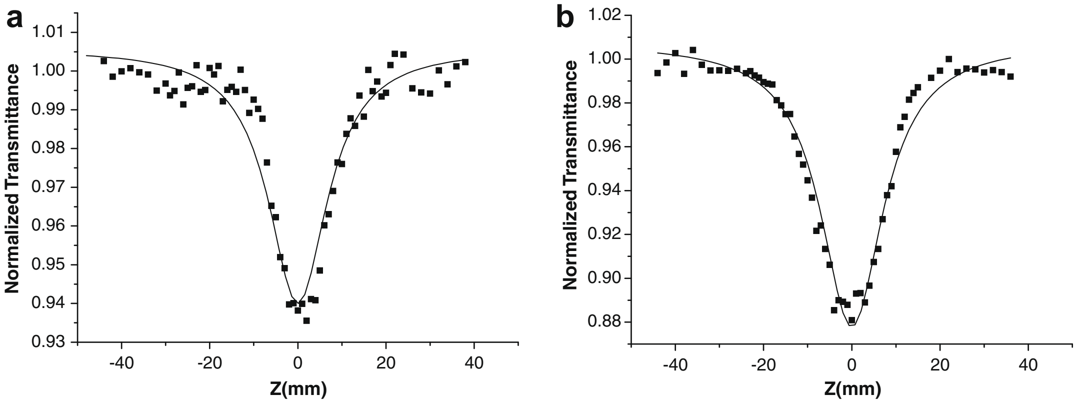


Fig. 5. Normalized transmittance data of open-aperture Z-scan for the complexes of NiQ_2 (a) and $Ni(AAMQ)_2$, (b) in DMSO solution (2×10^{-2} M). The solid lines were the fitting curves.

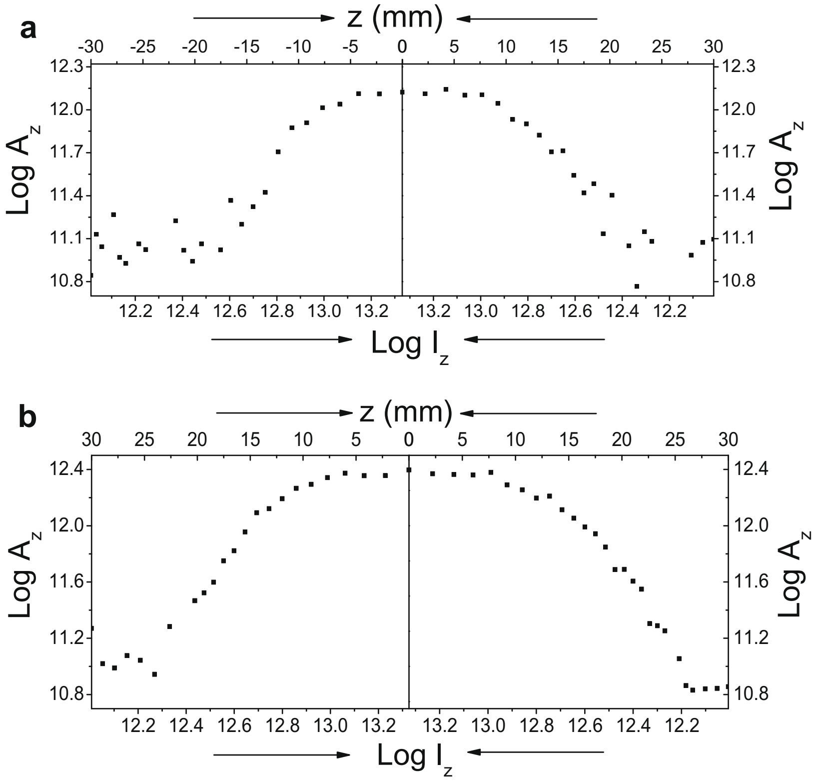


Fig. 6. Log (absorbed pulse energies vs. Log (the incident pulse energy (Log A_z – Log I_z) for NiQ_2 (a) and $Ni(AAMQ)_2$, (b) at different z positons.

Meanwhile, the transmittance data of open-aperture Z-scan for both compounds fitted relatively well with the two-photon absorption function (the solid curves in Fig. 5 were the theoretical fits). The transmittance (T_z) at z position related to two-photon absorption of a single beam was defined as [26]

$$T_z = \sum_{m=0}^{\infty} \frac{\left[-\frac{\beta I_0 L_{\mathrm{eff}}}{1+(z/z_0)^2}\right]^m}{(m+1)^{3/2}} \tag{4}$$

where $z_0 = \frac{\pi\omega_0^2}{\lambda}$ was the Rayleigh diffraction length.By fitting the experimental data according to Eq. (4) with the nonlinear absorption coefficient β and Rayleigh range z as free parameters, the nonlinear absorption coefficients β were determined to be 1.1×10^{-11} and 2.4×10^{-10} m/W, respectively for NiQ_2 and $Ni(AAMQ)_2$.The molecular TPA cross-section δ (in unit of cm^4 s/photon) could be calculated as

$$h\beta v = \delta N_A d_0 \times 10^{-3} \tag{5}$$

where h was the Planck constant, v was the frequency of incident laser, N_A was the Avogadro number, and d_0 was the concentration (in unit of mol/L).The third-order nonlinear absorption parameters were estimated for NiQ_2 and $Ni(AAMQ)_2$, as shown in Table 3, compared with some other reference compounds. It was worthy to note that the nonlinear absorption coefficient β of $Ni(AAMQ)_2$ was two times higher than that of NiQ_2, which was due to the change of the molecular electronic structure caused by substitution of the bulk acrylamidomethyl group to the 8-HQ ligand.

3.2.3. Effect of substituents on the NLO properties

Comparing the third-order nonlinear data of these two compounds, it was found that the nonlinear refraction properties were similar while the nonlinear absorption properties were obviously enhanced after the substitution of acrylamidomethyl group. Previous studies of structure–property relationship revealed that the TPA coefficient increased with the donor/acceptor strength, chain length and planarity of the π-center, and the TPA section would be increased with the extent of the charge transfer in the molecules [33].

For $Ni(AAMQ)_2$, λ_{max} of two absorption ranged at regions of 315–370 nm and 370–500 nm were both red shifted as compared to that of NiQ_2. For the intra-ligand transition, λ_{max} of $Ni(AAMQ)_2$ was 349 nm and λ_{max} of NiQ_2 was 346 nm. For the absorption ranged in 370–500 nm, it was assigned to a π–π^* ligand transition where charge density is transferred from oxygen to nitrogen [27]. Due to the characteristics of charge transfer, the bathchromic shift of this low-energy absorption band was more evident;

Table 3
Nonlinear absorption properties of nickel complexes of 8-HQ derivatives at 1064 nm.

Materials	β 10^{-11} m/W	$\chi_I^{(3)}$ 10^{-21} m^2/v^2	$\chi_I^{(3)}$ 10^{-13} esu	γ_I 10^{-46} m^5/v^2	γ_I 10^{-32} esu	δ GW	References
NiQ_2	1.1	6.5	4.6	1.6	1.2	5911	This work
$Ni(AAMQ)_2$	2.4	16	11	3.4	2.4	12,898	This work
$Ni_2(X{-}N{=}CHC_6H_4{-}o{-}O]_2$	–	–	–	–	1.4–66	–	Ref. [21]
Ni(R-Carbazole)$_2\cdot C_6H_6$	4.6×10^{-2}	–	–	–	–	285	Ref. [34]
$Ni_4O(MBT)_6$	7.8×10^{-2}	–	–	–	–	47,710	Ref. [35]

Table 4
Absorption maximum wavelengths and parameters of dipole moments of the ground states and the transition dipole moment of the excited states for NiQ_2 and $Ni(AAMQ)_2$.

Compound	μ_g [debye]	λ_{max}[nm]	μ_{g-e} [debye]
NiQ_2	0.0019 (0.0000, 0.0000, −0.0019)	341	1.30 (1.2806, −0.2063, 0.0001)
		407	1.33 (1.3169, −0.1468, 0.0000)
$Ni(AAMQ)_2$	0.1904 (−0.1844, 0.0383, −0.0279)	346	1.43 (−1.3864, −0.3544, −0.0023)
		419	1.58 (−1.5396, −0.3625, −0.0017)

$\lambda_{max} = 423$ nm for $Ni(AAMQ)_2$ while $\lambda_{max} = 415$ nm for NiQ_2. Consistently, the same trend was observed for absorption of their ligands; λ_{max} of AAMQ was 328 nm while λ_{max} of 8-HQ was 312 nm. The acrylamidomethyl group was unconjugatedly linked to the 8-HQ and the bathchromic shift in absorption could be attributed to the electron effect of the δ-donor group (CH_2) in the acrylamidomethyl substituents in the ligands, which could be viewed form the charge distribution in its HOMO molecular orbital. The participation of δ-donor group of CH_2 in the conjugation resulted in increased ligand-field strength. Thus the NLO responses would correspondingly increase. Moreover, the NLO property was strongly dependent on the absolute magnitude and orientation of the chromophore transition dipole moment [36,37]. The theoretical calculated results revealed that the $Ni(AAMQ)_2$ possessed a higher transition dipole moment due to contribution of δ-donor group of CH_2 to the whole molecular conjugation. Thus the NLO properties would accordingly respond. For the lowest excited state corresponded to the low-energy absorption at about 410 nm, the transition dipole moment for NiQ_2 was 1.30 D (Table 4). After introducing an acrylamidomethyl group to 5-position of 8-HQ ligand, the transition dipole moment of $Ni(AAMQ)_2$ was enhanced by about 19% (1.43 D). Such an increase in dipole moment, caused by participation of δ-donor group of CH_2 in the whole molecular conjugation, was crucial for enhancement in nonlinear absorption. As we have discussed above.

4. Conclusion

In this work, nickel complex of 5-(acrylamido)methyl-8-hydroxyquinoline, $Ni(AAMQ)_2$ has been synthesized and its nonlinear optical properties were investigated with respect to that of NiQ_2, by using the single beam Z-scan technique at 1064 nm. The real part and imaginary part of the molecular second-order hyperpolarizabilities (γ_R, γ_I) were estimated at molecule level, respectively. Both of the complexes obviously exhibited strong self-defocusing nonlinear refraction. Meanwhile, $Ni(AAMQ)_2$ revealed an enhanced TPA as compared to NiQ_2, which was attributed to the electron effect of substituents and the increased transition dipole moment caused by the participation of molecular conjugation of the δ-donor group (CH_2) in the acrylamidomethyl substituents on the 8-HQ ligands.

Acknowledgements

We sincerely express our thanks to the National Natural Science Foundation of China (Grant Nos. 20733007 and 50221201), the Natural Science Foundation of Jiangsu Province (Grant Nos. 08KJD150016 and 09KJB150009) and Natural Science Foundation of Nanjing University of Posts and Telecommunications (NUPT) (Grant No. NY207041) for the financial supports.

References

[1] M. Sheik-Bahae, A.A. Said, T.D. Wei, J. Hagan, E.W. Van Stryland, IEEE J. Quantum Electron. QE-26 (1990) 760.
[2] M.M. Bader, T. Hamada, A. Kakuta, J. Am. Chem. Soc. 114 (1992) 6475.
[3] M.M. Bader, Proc. SPIE 3473 (1998) 112.
[4] M.P. Cifuentes, C.E. Powell, M.G. Humphrey, G.A. Heath, M. Samoc, B. Luther, J. Phys. Chem. A 42 (2001) 9625.
[5] J.G. Breitzer, D.D. Dlott, L.K. Iwaki, S.M. Kirkpatrick, T.B. Rauchhfuss, J. Phys. Chem. A 103 (1999) 6930.
[6] K. Kamada, K. Ohta, Y. Shimoyama, T. Miyabayashi, K. Mashima, Opt. Mater. 27 (2004) 573.
[7] D.A. Parthenopoulos, P.M. Rentzepis, Science 245 (1989) 843.
[8] W. Denk, J.H. Strickler, W.W. Webb, Science 248 (1990) 73.
[9] J.D. Bhawalkar, G.S. He, C.-K. Park, C.F. Zhao, G. Ruland, P.N. Prasad, Opt. Commun. 124 (1996) 33.
[10] J.D. Bhawalkar, N.D. Kumar, C.F. Zhao, P.N. Prasad, J. Clin. Laser Med. Surg. 15 (1997) 201.
[11] (a) S. Maruo, O. Nakamura, S. Kawata, Opt. Lett. 22 (1997) 132;
(b) G.S. He, G.C. Xu, P.N. Prasad, B.A. Reinhardt, J.C. Bhatt, A.G. Dillard, Opt. Lett. 20 (1995) 435.
[12] A. Abbotto, L. Beverina, R. Bozio, A. Facchetti, C. Ferrante, G.A. Pagani, D. Pedron, R. Signorini, Chem. Commun. 17 (2003) 2144.
[13] O. Varnavski, X.Z. Yan, O. Mongin, M. Blanchard-Desce, T. Goodson, J. Phys. Chem. C 111 (2007) 149.
[14] C. Martineau, G. Lemercier, C. Andraud, Opt. Mater. 21 (2002) 555.
[15] Y. Li, J. Lu, J.Q. Xu, X.B. Cui, Y.H. Sun, K.C. Li, Q.X. Yang, L.Y. Pan, H.Y. Bie, Chem. Res. Chin. Univ. 20 (2004) 681.
[16] Q. Gan, S. Li, S. Wang, S. Shen, H. Xu, G. Yang, Opt. Express 13 (2005) 5424.
[17] S. Wang, Q. Gan, Y. Zhang, S. Li, H. Xu, G. Yang, ChemPhysChem 7 (2006) 935.
[18] A.A. Dakhel, Y.A.M. Ahmed, F.Z. Henari, Opt. Mater. 28 (2006) 925.
[19] I.R. Whittall, M.P. Cifuentes, M.G. Humphrey, Organometallics 16 (1997) 2631.
[20] J. Tedim, S. Patrício, R. Bessada, R. Morais, C. Sousa, M.B. Marques, C. Freire, Eur. J. Inorg. Chem. (2006) 3425.
[21] J.M. Floyd, G.M. Gray, A.G. Van, E. Spivey, C.M. Lawson, T.M. Pritchett, M.J. Ferry, R.C. Hoffman, A.G. Mott, Inorg. Chim. Acta 358 (2005) 3773.
[22] Analysis data of AAMQ: M.p. 167–169 °C. ^1H NMR (300 Hz, $CDCl_3$). $\delta = 8.81$ (1H, s), $\delta = 8.44$ (2H, d, $J = 8.1$), $\delta = 7.50–7.53$ (1H, m), $\delta = 7.42$ (1H, d, $J = 7.2$), $\delta = 7.11$ (1H, $J = 8.1$), $\delta = 6.35$ (1H, d, $J = 16.7$), $\delta = 6.05$ (1H, dd, $J = 10.2, 16.7$), $\delta = 5.68$ (2H, d, $J = 10.2$), $\delta = 4.89$ (2H, d, $J = 3.2$), ESI-MS, m/z: 229.1 $[M+H^+]$. Anal. Calc. for $C_{13}H_{12}N_2O_2$ (228.1): C, 68.41; H, 5.30; N, 12.27; Found: C 68.28, H 5.17, N 12.18.
[23] Analysis data of $Ni(AAMQ)_2$: M.p. above 300 °C. ^1H NMR (300 Hz, DMSO). $\delta = 8.62–8.64$ (4H, b), $\delta = 6.12–6.22$ (12H, b), $\delta = 5.53–5.55$ (6H, b), ESI-MS, m/z: 535.1 $[M+Na^+]$..
[24] E. Uhlemann, B. Opitz, U. Schilde, M. Raab, W. Kalies, Z. Anorg. Allg. Chem. 520 (1985) 167.
[25] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision A.1, Gaussian Inc., Pittsburgh, PA, 2003.
[26] P. Schaefer, H.H.E. Riehen, H.R.H. Basel, A.M. Muttenz, United States Patent US3391114, 1966.
[27] R. Ballardini, G. Varani, M.T. Indelli, F. Scandola, Inorg. Chem. 25 (1986) 3858.
[28] J.B. Willis, D.P. Mellor, Inorg. Chem. 69 (1947) 1237.
[29] H.A. Mackenzie, D.P. Mellor, J.E. Mills, L.N. Short, J. Proc. Roy. Soc. New South Wales 70 (1944) 70.
[30] K. Kamada, K. Ohta, Y. Shimoyama, T. Miyabayashi, K. Mashima, Opt. Mater. 27 (2004) 573.
[31] L. Rodríguez, C. Simos, J. Hernández, H. Gutierrez, M. Sylla, M. Giffard, A. Marcano, H. Soscun, X. Nguyen Phu, Opt. Mater. 27 (2004) 641.
[32] (a) R.A. Ganeev, A.I. Ryasnyansky, M. Baba, M. Suzuki, N. Ishizawa, M. Turu, S. Sakakibara, H. Kuroda, Appl. Phys. B 78 (2004) 433;
(b) Characterization of nonlinear refractive index materials, in: R.L. Sutherland (Ed.), Handbook of Nonlinear Optics, second ed., Basel, New York, 2003, pp. 436, 456–474.
[33] W.H. Lee, H . Lee, J.A. Kim, J.H. Choi, M. Cho, S.J. Jeon, B.R. Cho, J. Am. Chem. Soc. 123 (2001) 10658.
[34] S.L. Li, J.Y. Wu, Y.P. Tian, Y.W. Tang, M.H. Jiang, H.K. Fun, S. Chantrapromma, Opt. Mater. 28 (2006) 897.
[35] F.F. Jian, H.L. Xiao, Z.S. Bai, P.S. Zhao, J. Mater. Chem. 16 (2006) 3746.
[36] O. Prezhdo, Adv. Mater. 14 (2002) 597.
[37] Y. Chen, M. Hanack, Y. Arakic, O. Itoc, Chem. Soc. Rev. 34 (2005) 517.