Short communication

Synthesis, characterization and third-order nonlinear optical studies of copper complexes containing 1,10-phenanthroline-5,6-dione and triphenylphosphine ligands

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ABSTRACT

This research article describes the synthesis, characterization and third-order nonlinear optical studies of copper(I) complexes [Cu(Br)(N,N′-C$_{12}$H$_6$N$_2$O$_2$)(PPh$_3$)] and [Cu(I)(N,N′-C$_{12}$H$_6$N$_2$O$_2$)(PPh$_3$)] abbreviated as [CuBrLPPh$_3$] (1) and [CuILPPh$_3$] (2) (L = 1,10-phenanthroline-5,6-dione). Nonlinear optical properties of the complexes are investigated at 532 nm using single beam Z-scan and degenerate four-wave mixing (DFWM) techniques employing nanosecond laser pulses. The complexes show optical limiting behaviour due to "effective" two-photon absorption. The values of the effective two-photon absorption (2PA) coefficients (β), third-order nonlinear susceptibilities ($\chi^{(3)}$), and figures of merit (F), are calculated.

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1. Introduction

The development of new materials that exhibit nonlinear optical (NLO) response and have the potential for commercial device applications continues to be of primary interest in industrial and university laboratories [1]. Since the report in 1987 by Green et al. [2], in which good second-harmonic generation (SHG) efficiency was revealed for a ferrocenyl derivative, attention has been paid to the study of metal complexes as potential second-order NLO materials. Various classes of metal complexes have thus been systematically studied for new and optimised second order NLO activity. Review articles that have appeared in the last two decades on NLO metal complexes show the status of active research in this field [3–7]. Organometallic and coordination compounds have highly polarisable d-orbitals. In fact the ligand and metal orbitals can interact strongly, either in the ground or excited states, leading to highly polarizable compounds with good third order NLO properties. The metal–ligand interaction can be tuned by varying the metal atom, the oxidation state of the metal or the surrounding ligands. It should thus be possible to exploit the good electronic flexibility of

organometallic and coordination compounds to develop new third order NLO materials [8].

In the case of resonant excitation, excited state absorption (ESA) is a major contributor to nonlinear absorption. In transparent materials genuine two-photon absorption (TPA) can lead to the nonlinearity, which may sometimes induce a subsequent ESA as well. Optical materials exhibiting strong two-photon absorption (2PA) have recently received considerable attention due to their numerous potential applications, such as fluorescence imaging [9], up-conversion lasing [10] and optical limiting [11]. Nonlinearity due to ESA, induced by TPA or otherwise, has been demonstrated by nonlinear transmission and open-aperture (OA) Z-scan experiments [12] in many materials, including charge-transfer salts [13,14], nanocomposites [15] and organic molecules [16,17]. However, only a few reports have appeared in this regard on metal complexes [18,19].

Copper(I) is an important metal ion, which has a strong tendency to form covalent bonds with ligands containing S or P donor atoms [20–26]. 1,10-Phenanthroline-5,6-dione (L), is a more versatile molecule with numerous applications including the synthesis of materials showing interesting optical [27] and electrical properties [28–30]. Intramolecular electron transfer between the two redox sites of metals and ligands often generates characteristic CT bands that are regulated by external stimuli such as photo-irradiation,

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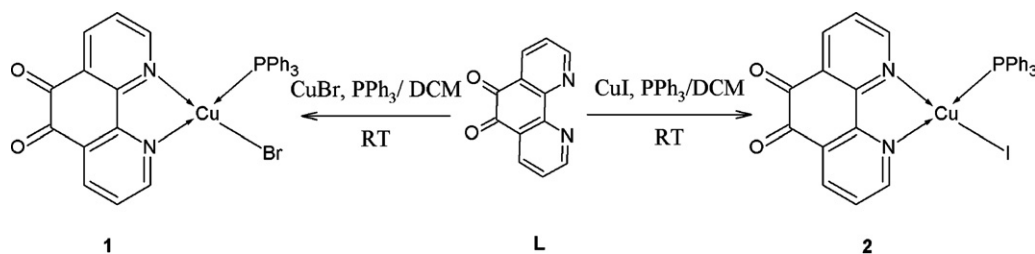
Scheme 1. Synthetic scheme for complexes 1 and 2.

heat reactions, and redox reactions. Therefore, metal complexes having redox active ligands are feasible candidates for molecular switchings [31]. Compounds which contain an electron donor and acceptor moiety are frequently characterized by charge transfer (CT) bands in their electronic spectra. Light absorption leads to charge separation which attracts much interest owing to important applications such as artificial photosynthesis [32] and nonlinear optical properties [33].

It should be quite interesting to modify an organic donor–acceptor molecule by placing a metal ion between the donor and acceptor which then become separate ligands. As a consequence an optical ligand-to-metal or metal-to ligand or ligand-to-ligand charge transfer (LLCT) [34,35] could exist. Based on this approach, we have synthesised and measured the third-order NLO properties of two new Cu(I) complexes with two electron withdrawing ligands (L and PPh$_3$) using the Z-scan and degenerate four-wave mixing (DFWM) techniques. The values obtained for the effective two-photon absorption (2PA) coefficients (β), third-order nonlinear susceptibilities ($\chi^{(3)}$) and figures of merit (F) are compared to those measured recently in other systems.

2. Experimental

2.1. Materials

All chemicals used were of analytical grade. Cuprous bromide, Cuprous iodide, 1,10-phenanthroline and triphenylphosphine were procured from Sigma–Aldrich. Literature method was used for the preparation of 1,10-phenanthroline-5,6-dione [36]. Elemental analyses were performed with a Flash EA, 1112 Series Elemental Analyser. Magnetochemical measurements were recorded on a Sherwood Scientific instrument (UK). FT-IR spectra were recorded on a Thermo Nicolet Avatar FT-IR spectrometer as KBr powder. UV–visible measurements were carried out in fiber optic spectrometer (model SD 2000, Ocean Optics Inc., USA) and corrected by subtracting solvent backgrounds. The ^{1}H and ^{31}P spectra were recorded using Bruker AV 400 spectrometer operating at the frequency of 400 MHz. The spectra were recorded in solution with DMSO as internal lock. DMSO and 85% H$_3$PO$_3$ were used as reference and external standards for ^{1}H and ^{31}P respectively.

NLO measurements were done using frequency-doubled Q-switched Nd:YAG lasers generating nanosecond laser pulses. The third-order optical nonlinearity of complexes 1 and 2 in DMF solution, at the concentration of 2.5 mmol/l, were measured by the Z-scan and DFWM techniques. At this concentration the solutions show a linear transmission of 55% and 48% respectively for complexes 1 and 2, at the excitation wavelength of 532 nm.

2.2. Synthesis of the complexes

2.2.1. [CuBrLPPh$_3$] (1)

CuBr (341 mg, 2.378 mmol) was added to the DCM (20 cm^3) solution of PPh$_3$ (623 mg, 2.378 mmol) and 1,10-phenanthroline-5,6-dione (500 mg, 2.378 mmol). After the reaction mixture was stirred 3 h at room temperature under nitrogen, the blackish brown solid formed was filtered off, washed with ethanol and Et$_2$O, dried under reduced pressure (Scheme 1). Yield: 70%, mp: >300 °C.

Anal. Calc for C$_{27}$H$_{21}$CuBrN$_2$P: C, 55.92; H, 3.62; N, 4.83; O, 5.51. Found: C, 57.43; H, 3.40; N, 4.48; O, 5.15%. NMR: δH (400 MHz; DMSO-d_6; referenced with respect to DMSO-d_6). There are two sets of aromatic protons found (^{1}H, 8.804–7.545, from L and ^{1}H, m, 7.539–7.368), from PPh$_3$ and δP (^{31}P, 28.54; referenced with respect to H$_3$PO$_4$) UV–vis: λ_{max}/nm (DMF) ~350 and 278.7 IR: ν_{max}/cm^{-1} (KBr) 1684.1 (C=O) [37], 1566.8 (C=N).

2.2.2. [CuILPPh$_3$] (2)

Synthesis of this complex is accomplished following a similar procedure taking CuI in place of CuBr (452 mg, 2.378 mmol). The blackish brown solid formed was filtered off, washed with ethanol and Et$_2$O, dried under reduced pressure (Scheme 1). Yield: 70%. mp: 300 °C.

Anal. Calc for C$_{30}$H$_{25}$CuIN$_2$P: C, 51.74; H, 3.35; N, 4.46; O, 5.10. Found: C, 53.26; H, 3.17; N, 4.19; O, 4.76%. NMR: δH (400 MHz; DMSO-d_6; referenced with respect to DMSO-d_6). There are two sets of aromatic protons (^{1}H, 8.804–7.545, from L and ^{1}H, m, 7.539–7.368), from PPh$_3$ and δP (^{31}P, 28.36; referenced with respect to H$_3$PO$_4$) UV–vis: λ_{max}/nm (DMF) ~350 and 278.3. IR: ν_{max}/cm^{-1} (KBr phase) 1679 (C=O) [37], 1569.1 (C=N).

2.3. Nonlinear optical studies

2.3.1. Z-scan measurement

Open-aperture Z-scan measurements were performed to determine the nonlinear transmission of laser light through the samples. The Z-scan is a widely used technique developed by Sheik-Bahae et al. [9] to measure optical nonlinearity of materials, and the open aperture Z-scan gives information about the nonlinear absorption coefficient. Here a laser beam is focused using a lens and passed through the sample. The beam's propagation direction is taken as the z-axis, and the focal point is taken as z = 0. The beam will have maximum energy density at the focus, which will symmetrically reduce towards either side for the positive and negative values of z. The experiment is done by placing the sample in the beam at different positions with respect to the focus (different values of z), and measuring the corresponding light transmission. The graph plotted between the sample position z and the normalized transmittance of the sample T (norm.) (transmission normalized to the linear transmission of the sample) is known as the Z-scan curve. The nonlinear absorption coefficient of the sample can be numerically calculated from the Z-scan curve. In our experiment, DMF solutions of the samples taken in 1 mm cuvettes were irradiated by plane polarized 5 ns laser pulses at 532 nm obtained from the second harmonic output of a Q-switched Nd:YAG laser (MiniLite, Continuum). The laser pulse energy was 160 micro Joules and the beam focal spot radius (ω_0) was 18 μm. These values yield a Rayleigh range (z_0) of 1.9 mm, and on-axis peak intensity (I_0) of 6.29 × 10^9 W/cm^2, for a spatially Gaussian beam. The laser was run in the single shot mode
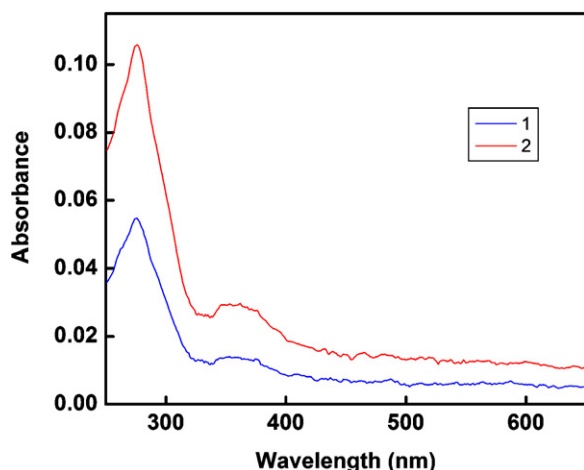
Fig. 1. The absorption spectra of complexes 1 and 2 in DMF.

Fig. 2. The open aperture Z-scan curve measured for complex 1. Filled circles are measured data points while the solid curve is the numerically calculated fit for a two-photon absorption process using Eq. (1).

using a data acquisition programme, with an approximate interval of 3–4 s between each pulse. This low repetition rate prevents sample damage and cumulative thermal effects in the medium.

2.3.2. DFWM measurement

Four-wave mixing refers to the interaction of four electromagnetic waves in a nonlinear optical medium via the third-order nonlinear polarization. When all the waves have the same frequency, it is called degenerate four-wave mixing (DFWM). Usually, the phase-conjugate and BOXCARS geometries are used for DFWM experiments. We used the forward folded BOXCARS geometry, where a laser beam is split into three and the beams are aligned such that they form three corners of a square. The diametrically opposite beams are the pump beams, and they have the same intensity. The third beam is the probe which has an intensity of about 20% of the pump beam. When the beams are focused onto the sample the fourth beam (signal beam) is generated due to nonlinear interaction, which will appear on the fourth corner of the square. It can be measured using a detector. For our DFWM experiment we used plane polarized 7 ns laser pulses at 532 nm obtained from the second harmonic output of a Q-switched Nd:YAG laser (Quanta Ray, Spectra Physics). A polarizer was used to change the intensity of the input laser beam. The input energy was monitored using a pyroelectric energy probe, and the generated signal beam was measured in the far field using a calibrated photodiode.

3. Results and discussion

3.1. Spectral analysis

The electronic spectra of the complexes (1 and 2) are given in Fig. 1. Spectrum of complexes is dominated by one main absorption band in the region 275–290 nm and a shoulder near 350 nm which are ascribed to the intra-ligand (π to π^*) transitions of triphenylphosphine. Also absence of bands (d–d) above 400 nm shows d^{10} electronic configuration of copper (Cu(I)) in the complexes. Since Cu(I) is reducing as well as oxidizing, MLCT and LMCT transitions will be occur at relatively low energies [38]. Free triphenylphosphine shows a broad band with λ_{max} at 262 nm [39]. The IR spectra of complexes 1 and 2 show absorption bands at $1684.1 \, cm^{-1}$ and $1679 \, cm^{-1}$ respectively, assigned to the CO stretching of L coordinated to the metal through the nitrogen atoms. These bands are slightly higher shifted wave number compared with free uncomplexed L ($1672 \, cm^{-1}$). The appearance of the $\nu(CO)$ bands (at $1684.1 \, cm^{-1}$ and $1679 \, cm^{-1}$) in the IR spectrum and the absence of bands in the region of 400–500 nm in the electronic

absorption spectrum of complexes (1 and 2) further confirms that L is bound to Cu(I) with the N,N′-chelate [31]. Magnetic susceptibility measurement show that the complexes are diamagnetic and copper is in +1 oxidation state. From the above spectral information, it was confirmed that structure of the complexes are distorted tetrahedral (d^{10}) and copper atom bonding with nitrogen atoms of 1,10-phenanthroline-5,6-dione (L).

3.2. Z-scan studies

The open aperture Z-scan curves of complexes 1 and 2 are given in Figs. 2 and 3 respectively. These show an increase in absorption when the sample is nearing the beam focus. Since the residual absorption of the samples at the excitation wavelength is in the vicinity of 50%, the nonlinearity can be expected to arise from a two-step or three-step excitation process involving real excited states, which essentially amounts to reverse saturable absorption (RSA). Genuine two-photon (2PA) and three-photon (3PA) absorption involving virtual states also can take place in the system, but these will be relatively weak compared to the RSA process. However, an excitation where two photons are involved will numerically fit to a two-photon absorption equation irrespective of whether real or virtual states are involved. Similarly, if three photons are involved, it will fit to a three-photon absorption equation. Therefore we tried to fit our data to two-photon and three-photon equations, and the
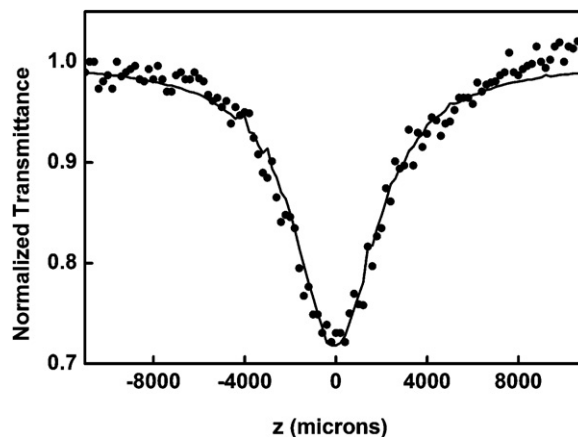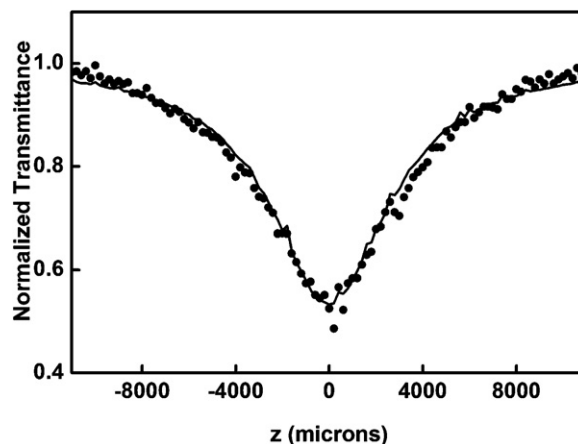

Fig. 3. The open aperture Z-scan curve measured for complex 2. Filled circles are measured data points while the solid curve is the numerically calculated fit for a two-photon absorption process using Eq. (1).
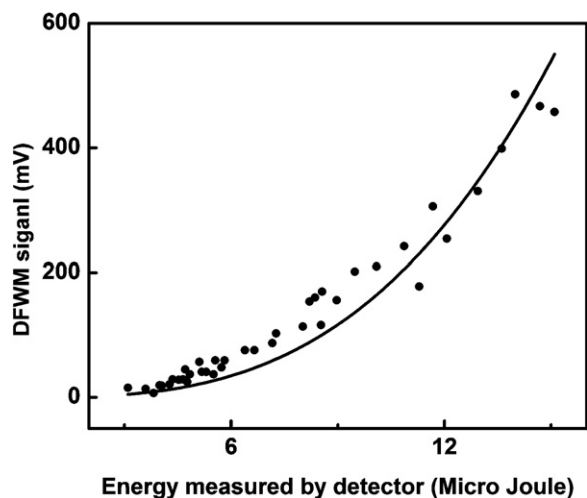
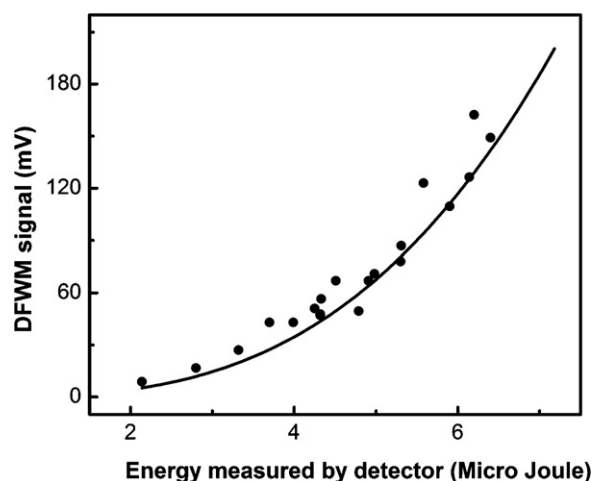**Fig. 4.** DFWM signal versus pump energy for complex 1.

Fig. 5. DFWM signal versus pump energy for complex 2.

best fit was obtained to the two-photon process described by the nonlinear transmission equation [40]

$$T = \left(\frac{(1-R)^2 \exp(-\alpha L)}{\sqrt{\pi q_0}} \right) \int_{-\infty}^{\infty} \ln \left[\sqrt{1 + q_0 \exp(-t^2)} \right] \, dt \qquad (1)$$

where T is the actual z-dependent sample transmission (product of linear transmission and normalized transmittance), and L and R are the length and surface reflectivity of the sample respectively. a is the linear absorption coefficient. q_0 is given by $\beta(1-R)I_0 L_{eff}$, where β is the two-photon absorption coefficient, and I_0 is the on-axis peak intensity. L_{eff} is given by $1 - \exp(-\alpha l/\alpha)$. The quantity β here is the *effective* 2PA coefficient, as it is a lumped coefficient for the effects of RSA as well as genuine 2PA. The β values of complexes 1 and 2 are found to be 2.4×10^{-11} m/W and 7.7×10^{-11} m/W respectively. For comparison, under similar excitation conditions, the NLO materials Cu nanocomposite glasses [41] and Schiff base complexes of N,N′-bis(2-hydroxynaphthalidene)phenylene-1,2-diamine ligand with metal M (M = Ni(II), Zn(II) and Fe (III)) [42] had given effective 2PA coefficient values of 10^{-1} to 10^{-12} m/W. Similarly, Bismuth nanorods [43] and CdS quantum dots [44] gave values of 5.3×10^{-11} m/W and 1.9×10^{-9} m/W respectively. In all these materials strong excited state absorption was found to happen concurrently with genuine 2PA, since the samples used had some residual absorption at the excitation wavelength of 532 nm.

3.3. DFWM studies

The DFWM process can be interpreted by two different theoretical models, namely the four-photon parametric interaction model and the induced grating model [45]. The former is applicable when the third-order nonlinear polarization is caused by electronic cloud distortion or intramolecular motion. It may be noted that strong intramolecular charge transfer excitations (MLCT, LMCT, ILCT) exist in these complexes [31,38,46]. The latter model is more general, and can be applied to various experimental conditions and mechanisms involving molecular reorientation, electrostriction, population change and the thermo-optical effect. In our case the samples have residual absorption, resulting in population change and thermal effects upon excitation. These effects, together with the intramolecular excitations, are hence responsible for generating the DFWM signal beam in the present case.

The variation of the measured DFWM signal as a function of pump intensity for complexes 1 and 2 are shown in Figs. 4 and 5, respectively. The signal is proportional to the cubic power of the

Table 1
The values of β, α, F, and $\chi^{(3)}$ measured for complexes 1 and 2.

Complex	Z-scan	α (cm^{-1})	DFWM	
	β (m/W)		F (e.s.u.-cm)	$\chi^{(3)}$ (e.s.u.)
1	2.4×10^{-11}	5.98	2.5×10^{-12}	1.5×10^{-11}
2	7.7×10^{-11}	7.34	6.8×10^{-12}	5.0×10^{-11}

input intensity as given by Eq. (2),

$$I(\omega)\alpha \left(\frac{\omega}{2\varepsilon_0 c n^2} \right) \left| \chi^{(3)} \right|^2 l^2 I_0^3(\omega) \qquad (2)$$

where $I(\omega)$ is the DFWM signal intensity, $I_0(\omega)$ is the pump intensity, l is the length of the sample, and n is the refractive index of the medium. The solid curves in the figures are the cubic fits to the experimental data $\chi^{(3)}$ can be calculated from Eq. (3),

$$\chi^{(3)} = \chi_R^{(3)} \left[\frac{I/I_0^3}{(I/I_0^3)_R} \right]^{1/2} \left[\frac{n}{n_R} \right]^2 \frac{l_R}{l} \left(\frac{\alpha l}{(1 - e^{-\alpha l}) e^{-\alpha l/2}} \right) \qquad (3)$$

where the subscript R refers to the standard reference, CS$_2$. $\chi_R^{(3)}$ is taken to be 9.5×10^{-21} m^2/V [47]. The figure of merit F, given by $\chi^{(3)}/\alpha$, is then calculated. F is a measure of nonlinear response that can be achieved for a given absorption loss in the medium. The F value is useful for comparing the nonlinearity of different materials when excited in spectral regions of nonzero absorption. Table 1 summarizes results obtained from the Z-scan and DFWM measurements. The F values obtained for complexes 1 and 2 are better compared to those obtained for conjugated polymers studied under similar experimental conditions [48].

4. Conclusions

In this paper we have reported the synthesis of two new copper(I) complexes using the electron acceptor ligands L and PPh$_3$, in which the electronic communication between the ligands happen through the metal (Cu(I)) ion. From analytical and spectral studies, a distorted tetrahedral structure has been assigned to the complexes. Being a polarizable molecular system with π-conjugated pathways having an asymmetric charge distribution, strong intramolecular charge transfer excitations exist in these compounds. These contribute substantially to the observed nonlinearity. The high thermal stability and large optical nonlinearity of these complexes make them potential candidates for photonic applications.

Acknowledgements

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