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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′-$C_{12}H_6N_2O_2$)(PPh_3)] and [Cu(I)(N,N′-$C_{12}H_6N_2O_2$)(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.

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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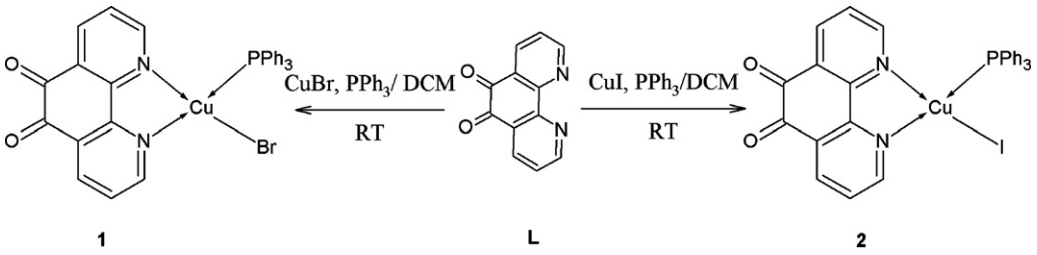

Scheme 1. Synthetic scheme for complexes 1 and 2.

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 ^1H 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_3PO_3 were used as reference and external standards for ^1H 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_2O, dried under reduced pressure (Scheme 1). Yield: 70%, mp: >300 °C.

Anal. Calc for $C_{27}H_{21}CuBrN_2P$: 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 (^1H, 8.804–7.545, from L and ^1H, m, 7.539–7.368), from PPh_3 and δP (^{31}P, 28.54; referenced with respect to H_3PO_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_2O, dried under reduced pressure (Scheme 1). Yield: 70%. mp: 300 °C.

Anal. Calc for $C_{30}H_{25}CuIN_2P$: 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 (^1H, 8.804–7.545, from L and ^1H, m, 7.539–7.368), from PPh_3 and δP (^{31}P, 28.36; referenced with respect to H_3PO_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