Ultrafast optical response of a new metal organic complex-polymer composite film

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Abstract: A new Cu-based metal organic complex incorporated into poly (methyl mathacrylate) film exhibits large and fast offresonant optical nonlinearity in the 800 to 1550 nm wavelength range. A large $\chi^{(3)}$ value of 1.8×10^{-10} esu is estimated.

Keywords: Nonlinear optics, Metal organic complex, Z-scan, Optical Kerr effect

1. Introduction

Metal-organic complexes bearing noble and transition metal atoms have gained much interest as nonlinear optical (NLO) materials because of their architectural flexibility with a variety of combinations of central metals and ligands as well as the charge-transfer nature of the metal–ligand bonds, which enhances the optical nonlinearity [1]. While both organometallic and coordination compounds constitute the class of metal complexes, the fundamental difference, by definition, is that the complex should possess at least one metal-carbon bond for it to be called as an organometallic complex. These materials possess additional advantages in that they can be grown as crystals as well as be incorporated into polymers such as poly (methyl methacrylate) (PMMA) to fabricate films. Broadband optical response in the infrared (IR) range is of growing interest for optical communication applications. Herein, we report on the broadband, large nonresonant optical nonlinearities of a new metal organic complex bearing a Cu atom, bis(1,10-phenanthroline) Copper(I) chloride, incorporated into PMMA film, in the wavelength range of 800 to 1550 nm. The results reveal its potential for all-optical applications.

2. Experiments

Differential optical Kerr gate (DOKG) [2] method with a femtosecond Ti:sapphire laser was used to investigate the third-order nonlinear optical susceptibility and the nonlinear response of the composite thin film. The laser beam from a Ti:sapphire laser, delivering 90 fs pulses at 800 nm at a repetition rate of 92 MHz, was divided into pump and probe beams with 20:1 intensity ratio by a beam splitter. The polarization of the probe beam was set to 45˚ with respect to that of the pump beam by a half wave plate. Two beams were focused on the sample by a convex lens of focal length of 7 cm. The time delay of the probe with respect to the pump was controlled by a PC-driven linear translator (PI, M-014.D01). At zero delay position, the pulses of the two beams overlap spatially and temporally, and the probe beam polarization rotates due to the birefringence induced in the sample by the pump beam. The pump beam, after passing through the sample, was blocked and the probe beam was passed through a quarter wave plate. The circularly polarized probe beam was then split in to two beams by a polarizing cube beam splitter and the two beams were detected by a photodetector pair connected to a lock-in amplifier. CS_2 was used as the reference material in the experiment. Single beam z-scan technique [2] employing the Ti:sapphire laser operating in the 800 to 1550 nm wavelength range (150-320 fs, 80 MHz) was used to investigate the third-order nonlinearity of the composite over a wide wavelength range. The laser beam was focused by a convex lens (f = 10 cm) on the sample. The beam waist at 800, 1250 and 1550 nm was measured to be 16, 18, and 20 μm, respectively.

To prepare the composite film, 2 mg of compound and 250 mg of PMMA (140,000 Mw) were dissolved in 2.5 mL of dichlorobenzene and mixed well with stirring. The concentration of the compound in solution was $1x10^{-3}$ mol/L. The solution was then uniformly spin coated onto the glass substrate at 1200 rpm for 90 s at room temperature. The film was dried in a vacuum oven at 100 ˚C for about 20 h.

3. Results and Discussion

Fig. 1 shows the structure of the new coordination complex and the linear absorption curve of its composite with PMMA. The composite is very transparent above 800 nm. The film thickness was found to be 1.28 μm using an Alpha Step surface profiler. In Fig. 2, the result of DOKG experiment performed at 800 nm is depicted. Optical Kerr signal is symmetric about the zero time delay indicating a fast response time of the composite, comparable to or shorter than the pulse width (90 fs). The data is fitted to a Gaussian function (solid line). The value of $\chi^{(3)}$ is estimated to be $1.8x10^{-10}$ esu, using the equation given in the literature [2]. This ultrafast nonlinear response originates from the

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conjugated π-electron system of ligands and is also influenced by metal-ligand interactions.

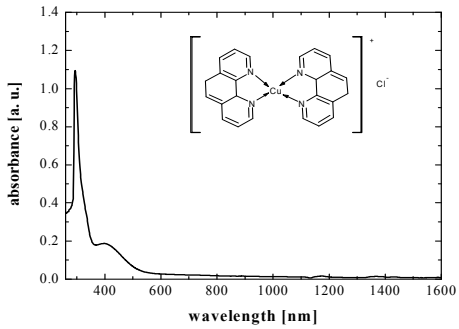

Fig. 1. Linear absorption of the composite. Shown inset is the molecular structure of the new coordination complex.

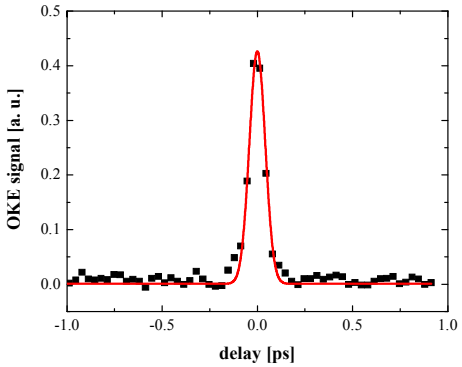

Fig. 2. Optical Kerr signal of the composite film at 800 nm.

Open aperture z-scan results at 800 nm at different input average power levels are displayed in Fig. 3. The effective value of two-photon absorption coefficient (β_{eff}) is found to be 510 cm/GW (at 0.32 GW/cm^2). Three-photon absorption (3PA) was found to occur at high intensities (8.7 GW/cm^2), by fitting the data to an equation describing the 3PA [2]. The 3PA coefficient was estimated to be 3.4 cm^3/GW^2.

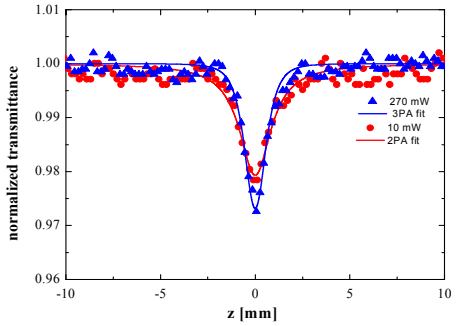

Fig. 3. 2PA at 10 mW (0.32 GW/cm^2) and 3PA at 270 mW (8.7 GW/cm^2) at 800 nm.

The results of nonlinear absorption at 1250 and 1550 nm at 270 mW of average power are shown in Fig. 4. Solid lines in Figs. 3 and 4 are the fits of data to equations given in Ref. 2, considering the corresponding Rayleigh range at each wavelength. The value of 2PA coefficient β at 1250 and 1550 nm is 88 and 41 cm/GW, respectively, at 270 mW (~3.3 GW/cm^2).

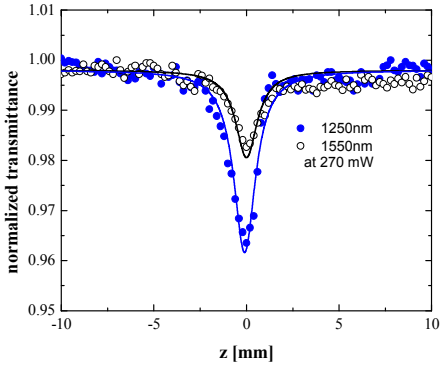

Fig. 4. 2PA at 1250 and 1550 nm. Solid lines are fits of data.

The metal complex shows two absorption peaks at 268 and 386 nm due to the intra ligand transition (π-π*) and the metal (d^{10}) to ligand charge transfer transition (MLCT), respectively. The composite film has an absorption tail in 580 to 800 nm range (Fig. 1). This indicates a possible partial contribution from one-photon transition to the nonlinear absorption near 800 nm and also a possible instantaneous 2PA in the range 1200 to 1600 nm. There can be resonant three- and four-photon absorption respectively at 1250 and 1550 nm at high intensity levels. However, they were not evident in the present study within the input intensity levels achievable with the laser output power. A comparable observation of 2P and 3PA in the IR spectral region is reported for solutions of fluorine-containing ferrocene derivatives in chloroform [3]. The values of β_{eff} and $\chi^{(3)}$ of the composite are much larger than those of other Cu based coordination compounds in solutions measured near 720 nm [4].

Overall, the new Cu-based coordination compound in PMMA film exhibits ultrafast and large optical nonlinearity in the IR region. The compound is thermally stable up to 250˚C and exhibits no laser damage in the intensity range involved in the experiments. Present results are interesting and they indicate the potential of this compound for applications demanding large 2PA, such as multi-photon microscopy, data storage and optical limiting [5].

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