Synthesis, spectroscopic and nonlinear characterization of 1,1′-(Ethylene-1,2-diyl)dipyridinium dichlorodinitratocuprate(II)

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The new organic-inorganic hybrid salt: 1,1'-(Ethylene-1,2-diyl)dipyridinium dichlorodinitratocuprate(II) was synthesized and characterized using UV-Vis, FTIR and NMR techniques. The nonlinear optical properties and optical switching were investigated using z-scan technique with CW laser beams at λ=532 and 635 nm. Theoretical fitting was performed to the recorded experimental data to calculate the nonlinear optical parameters including the thermo-optic coefficient calculations. The results have confirmed that the studied sample exhibited revers saturation absorption processes. The thermal lens effect was demonstrated all optical switching for the new organic-inorganic hybrid salt. The reported results led to possible potential applications of the studied complex in future promising optoelectronic applications.

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Keywords: Cross phase modulation, Organic-inorganic hybrid salt, Nonlinear coefficients

1. Introduction

A large number of organic and organo-metallic materials were interesting for exhibiting large nonlinear effects. These effects make such materials to be used within future photonic applications [1-3]. Most of the reported works were carried out to study the NLO properties of dyes, organic and organo-metallic materials [4-11]. Relating to all optical switching case, new materials have been investigated using pump- probe beams z- scan technique [12-13]. The conducted results led to some information on the cross-phase modulation (XPM), which is indicated to the change in the optical phase of a laser beam caused by the interaction with another beam inside the nonlinear medium. The benzenesulfonamide azo dye has been investigated and shown the thermal lens effect [14]. As well as, the switching behavior measurement of zinc phthalocyanine dye was reported [15]. All optical switching was demonstrated of the 3,4-pyridinediamine and revealed that the time of switch-on and switch-off of the 3,4-pyridinediamine was determined in μs range for the pump intensity [16].

This article reports the investigation of NLO properties of the new organic-inorganic hybrid salt: 1,1′-(Ethylene-1,2-diyl)dipyridinium dichlorodinitratocuprate(II) solution at two wavelengths λ= 532 nm and λ= 635 nm using z- scan technique with a pump-probe beams.

The added value of this work is to evaluate the two figures of merit of the nonlinear optical coefficients of the new organic-inorganic hybrid salt, in order to be used in future photonic applications. To our knowledge, the 1,1′-(Ethylene-1,2-diyl)dipyridinium dichlorodinitratocuprate(II) has been previously neither synthesized nor investigated on the bases on the nonlinear optical properties.

2. Experimental techniques

2.1. Materials and methods

Reactions and manipulations were achieved in air with reagent grade solvents. $Cu(NO_3)_2.3H_2O$ (BDH, Germany) is a commercial and it is used without any purification. $[C_{12}H_{14}N_2]Cl_2{\cdot}2H_2O$ was prepared according to reported literature method [17]. ^1H and $^{13}C\{^1H\}$ NMR spectra were taken on a "Bruker Bio spin 400 spectrometer ". As well as the FTIR spectra were recorded on "*Jasco* 2400 FTIR spectrometer" taken as KBr disk with a resolution of 4 cm^{-1}. Microanalysis was performed using *EURO EA* (Italy).

2.2. Synthesis of 1,1′-(Ethylene-1,2-diyl)dipyridinium dichlorodinitratocuprate(II)

An aqueous solution of $Cu(NO_3)2{\cdot}3H_2O$ (0.28 g, 1.15 mmol, 3 ml H_2O) was added to a solution of $[C_{12}H_{14}N_2]Cl_2{\cdot}2H_2O$ (0.34 g, 1.15 mmol, 3 ml of H_2O). Immediately, its color changed from blue into pale green. Then, the mixture was heated at 60°C for three hours. The solvent was then evaporated in vacuo to give quantitatively $[C_{12}H_{14}N_2][CuCl_2(NO_3)_2]$, which was washed with EtOH to give a faint green powder (450 mg, yield 90%).

2.3. Spectroscopic data

The organic-inorganic hybrid salt $[C_{12}H_{14}N_2][CuCl_2(NO_3)_2]$ (Fig. 1) was prepared by treatment of two equivalents $[C_{12}H_{14}N_2]Cl_2{\cdot}2H_2O$ with $Cu(NO_3)_2$ in an aqueous solution at ambient temperature. The green powdery salt is purely isolated, which has a

good solubility in water or dimethyl sulfoxide (DMSO), but it is poorly soluble in common organic solvents (chloroform, pyridine or ethanol). The composition and properties of the obtained salt are summarized in Table 1.

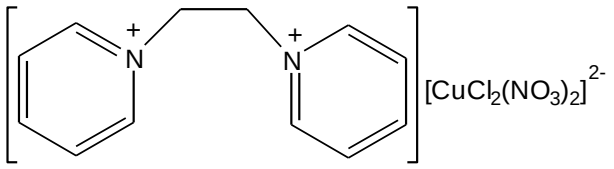

Fig. 1. Molecular structure of $[C_{12}H_{14}N_2][CuCl_2(NO_3)_2]$

Table 1. Characterization data of $[C_{12}H_{14}N_2][CuCl_2(NO_3)_2]$

Formula	M_r	w_i(calc.)/% w_i(found)/%			Yield	M.p.
		C	H	N	%	°C
$C_{12}H_{14}Cl_2N_4CuO_6$	444.72	32.41	3.17	12.60	80	140
		33.37	3.89	12.81		

2.4. Multinuclear, NMR, FTIR and UV-Vis characterizations

The ^1H and $^{13}C\{^1H\}$ NMR spectra for $[C_{12}H_{14}N_2][CuCl_2(NO_3)_2]$ (Fig. 2) have similar features to their corresponding ones of the structurally related salts $[C_{12}H_{14}N_2]Cl_2{\cdot}2H_2O$ [17] and $[C_{12}H_{14}N_2][Cu(NO_3)_4]$[18]. The observed ^1H NMR spectrum has shown four resonances (broadening peaks) corresponding to four different proton environments, the obtained peaks are in their expected Chemical shifts and relative intensity ratio. Broadening peaks are also observed in ^1H NMR spectra of the $[(C_5H_5N)_2CH_2][CuX_4]$ (X= Cl or NO_3),[19-20] which most probably due to the electric quadruple effects of the paramagnetic Cu(II)) centres in the complex. The $^{13}C\{^1H\}$ NMR spectrum also gave the predicted four resonances consistent with four environmentally different C centres. The NMR spectroscopic data are presented in Table 2.

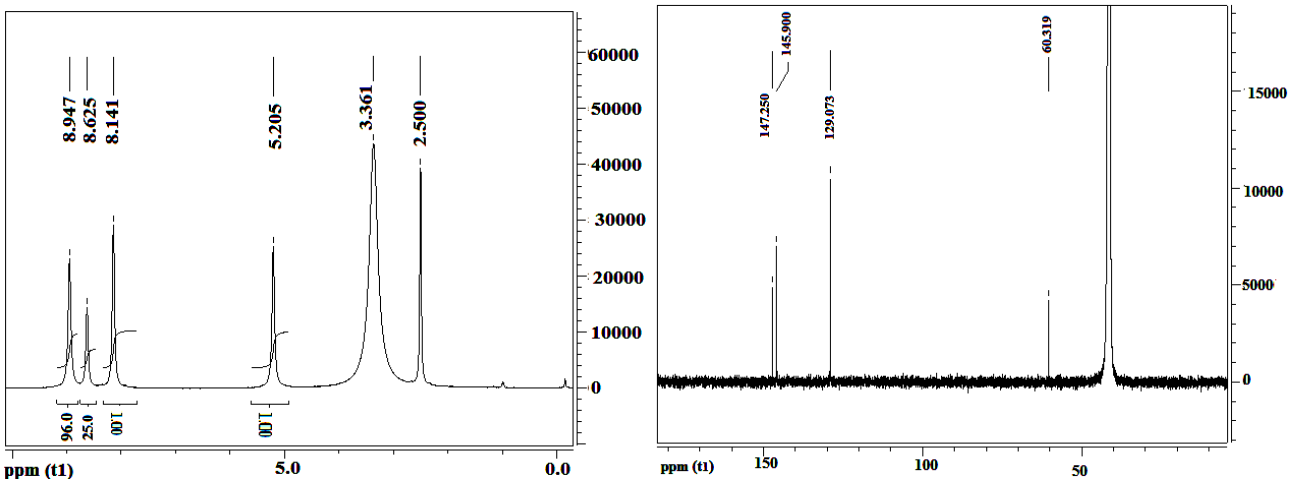

Fig. 2. ^1H (above) and $^{13}C\{^1H\}$NMR (below) spectra of $[C_{12}H_{14}N_2][CuCl_2(NO_3)_2]$ (DMSO, 25°C)

Table 2. The NMR spectroscopic data of $[C_{12}H_{14}N_2][CuCl_2(NO_3)_2]$

Spectral data
^1H NMR (DMSO-d_6), δ: 5.20 (b, 4H, CH_2), 8.14 (b, 4H, py), 8.62 (m, 2H, py), 8.95 (b, 4H, py)
$^{13}C\{^1H\}$ NMR (DMSO-d_6), δ: 60.32 (s, CH_2), 129.07 (s, Py), 146.90 (s, Py), 147.25 (s, Py)

The FTIR spectrum (Fig. 3) exhibits a characteristic band at 1386 cm^{-1}, which is readily assigned to the NO_3^- groups [19], while the distinctive absorption band at 1632 cm^{-1} is characteristic of C=N group. The relatively strong absorption frequency at 1481 cm^{-1} is assigned to CH_2 (def). The characteristic absorption frequencies of $[C_{12}H_{14}N_2][CuCl_2(NO_3)_2]$ are shown in Table 3.

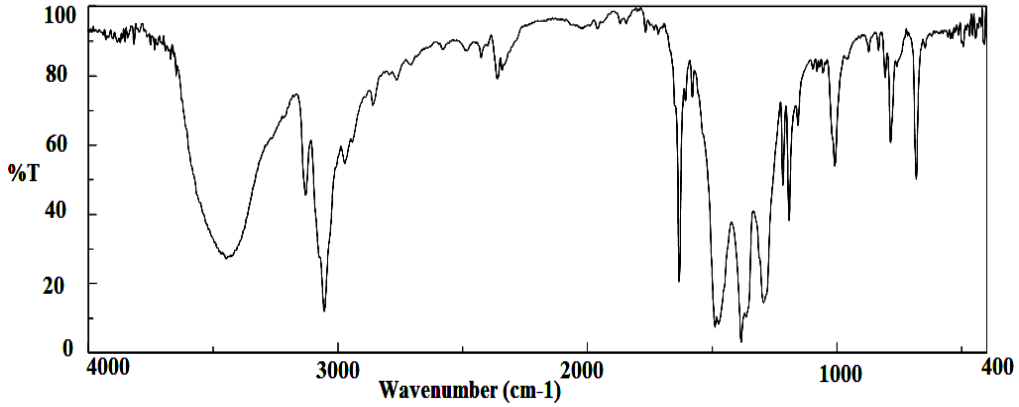

Fig. 3. FTIR spectrum of $[C_{12}H_{14}N_2][CuCl_2(NO_3)_2]$ (KBr disc)

Table 3. The IR frequencies (cm^{-1}) of $[C_{12}H_{14}N_2][CuCl_2(NO_3)_2]$

ν(C=N) *(str)*	ν(C–N) *(str)*	ν(CH_2) *(def)*	ν(NO_3) *(str)*
1632	1191	1481, 784	1386

The UV-Vis spectrum of the 1,1′-(Ethylene-1,2-diyl)dipyridinium dichlorodinitratocuprate(II) complex $[C_{12}H_{14}N_2][CuCl_2(NO_3)_2]$ was taken in the DMSO solution and this solution has been used as reference in all measurements. The recorded spectrum was in the range of 250-800 nm by the "UV-1601 PC Shimadzu Spectrophotometer". Fig. 4 shows a broad absorption band between 250 nm and 400 nm. This broad band can be assigned mainly to π →π* and d→d* transitions or ligand-to-metal charge-transfer (LMCT) in the inorganic part $[Cu(NO_3)_4]$ of the complex[21].

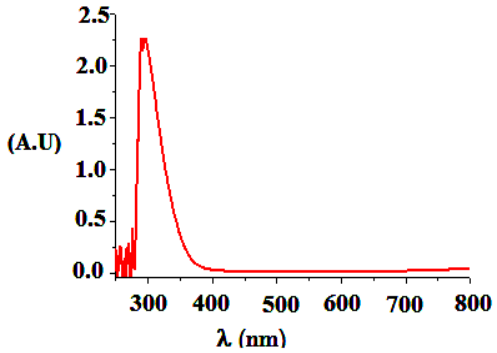

Fig. 4. UV-Vis spectrum of $[C_{12}H_{14}N_2][CuCl_2(NO_3)_2]$. complex in the DMSO solvent (color online)

2.5. Z-scan measurements

Single beam z-scan technique was used to estimate the nonlinear absorption coefficient "β" and the nonlinear refractive index "n_2". The used experimental setup was similar to our previous work [22]. Two types of laser were employed as excitation sources. The first source was a **CUBE™** diode laser with TEM_{00} Gaussian beam (Coherent-635-3QE, λ= 635 nm; the power was tuned up to 26 mW. The second laser source was CW diode laser with λ= 532 nm; the power is tuned up to 500 mW. The used laser beam was focused with a 10 cm lens that generated a beam waist of 29.5 μm with Rayleigh length of 5.13 mm, which was giving a power density of 1.4 MW/cm^2 for the green laser, and for the red laser, the beam waist of 35.2 μm with Rayleigh length of 6 mm giving a power density of 1.01 MW/cm^2. The sample cell can move through the focus area of laser beam by x-y translational stage connected to a computer-controlled. The z-scan measurements in an open/closed aperture configurations were carried out to measure the NLO coefficients "β"and the "n_2". The samples were prepared by taking an accurately weighed amount of the new complex and dissolved in DMSO with concentrations of 10^{-3}M.

2.6. Pump-probe set up for optical switching study

All Optical switching behavior of the (1,1′-(Ethylene-1,2-diyl)dipyridinium dichlorodinitratocuprate(II) was studied with the z-scan pump-probe technique. The first laser with λ=532 nm was used as pump laser to enhance the nonlinear effect. While, the probe beam (low power diode laser, with λ=635 nm and 0.5mW) was used to scan the sample for its nonlinear optical switching characteristics. The intensity of the probe beam is kept constant. The probe-pump beams signals were detected by two silicon photo detectors (Thorlab, DET-110), which connected to oscilloscope (Tektronics TDS-2024). The Schematic diagram of the experimental setup is shown in Fig. 5.

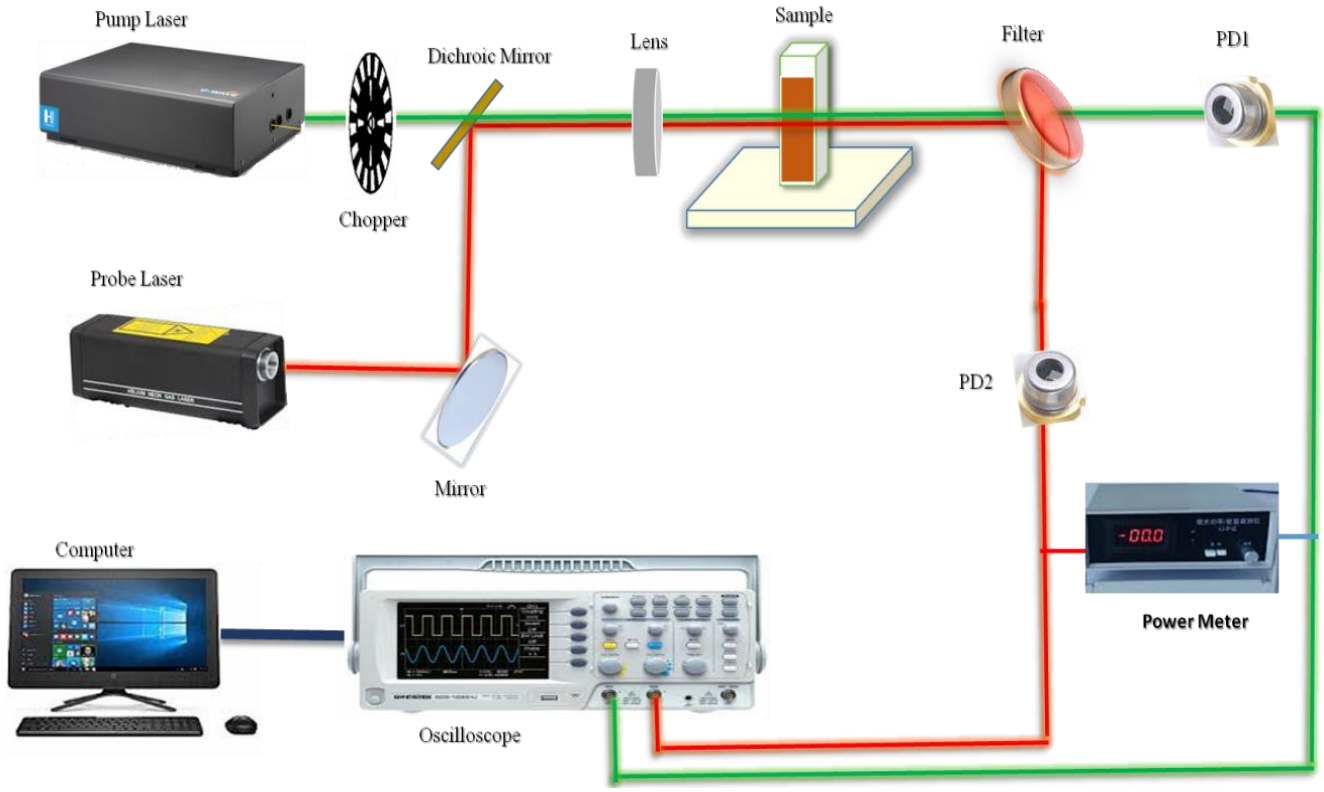

Fig. 5. The pump-probe experimental setup for optical switching measurements (color online)

3. Results and discussion

3.1. Z-scan measurements outcomes

Open aperture (OA) z-scan set-up was performed in order to estimate the nonlinear absorption coefficient "β" of 1,1′-(Ethylene-1,2-diyl) dipyridinium dichlorodinitratocuprate(II) in DMSO solution with a concentration of $10^{-3}M$. Fig. 6 shows the open aperture z-scan of 1,1′-(Ethylene-1,2-diyl) dipyridinium dichlorodinitratocuprate(II) in DMSO at two wavelengths, λ= 532 nm and λ= 635 nm. It seems that the shape of the curves is symmetrical (smooth valley) with respect to focal point (z=0), this confirms a strong nonlinear absorption (NL) mechanism happened such as: the reverse saturable absorption (RSA) processes to occur in our sample.

As concluded from Fig. 6 that our sample exhibited RSA mechanism, which means the $\sigma_{ex} >> \sigma_g$ condition should be satisfied, where σ_g is the cross-section of the ground state and σ_{ex} is the cross-section of the excited state. We have calculated the σ_{ex} and σ_g at wavelengths λ= 532 nm and λ= 635 nm using similar method [23-24], the obtained results confirmed that σ_{ex} is larger than σ_g and they are tabulated in Table 4. However, our results show that the σ_{ex} is five times larger than the σ_g for the wavelength of λ= 635 nm. And six times for the wavelength of λ= 532 nm, this suggests that the observed NL absorption is due to RSA process [25]. Theoretical fit to the experimental data "using the relation $T(z) = 1 - \frac{(I_0 L_{eff} \beta)}{[2^{\frac{3}{2}}(1+\frac{z^2}{z_0^2})]}$ in Fig. 6 have been performed with similar method reported in full details in ref. [23]. The results of calculating the NLA coefficient (β) is listed in Table 5.

The closed-aperture (CA) scan of our sample is performed to calculate the nonlinear refractive index "n_2". Figure 7 shows pure experimental data (CA/OA) of the studied sample in DMSO solution at two wavelengths, λ= 532 nm and λ= 635 nm. However, it important to mention that the effect of component "β" was eliminated using the division method [24].

The NL phase shift "$\Delta\phi_0$" was obtained from the fitting of the experimental recorded data in Fig. 7. Then, it is inserted in the following relation [$n_2 = \frac{\lambda \Delta\phi_0}{2\pi I_0 L_{eff}}$] to find the value of n_2.

The third-order nonlinear susceptibility (χ^3) is calculated from the two parts of real Re(χ^3) and the imaginary Im(χ^3) [22]:

$$|\chi^3| = [\mathrm{Re}(\chi^3)^2 + \mathrm{Im}(\chi^3)^2]^{1/2} \quad (1)$$

Both values of α_0 and n_0 are determined using similar method described in ref.[23]. The optical conductivity $[\sigma_{opt} = \frac{\alpha_0 n_0 c}{4\pi}]$ and the electrical conductivity $[\sigma_e = \frac{2\lambda \sigma_{opt}}{\alpha_0}]$ are calculated, the previous calculat-

ed parameters are listed in Table 4. As well as, the values of n_2, β, |Re χ^3| and |Im χ^3| are also presented in Table 5.

As CW laser is used here, the optical nonlinearity in the samples is raised from the thermal origin; this means that the refractive index depends on the temperature variation. In the present case, our sample is considered to be as self-defocusing material at λ= 532 nm and λ=635nm. The defocusing effect is due to thermal nonlinearity rising from absorption of tightly CW laser beam propagating through an absorbing sample solution producing a spatial distribution of temperature. The change in the n_2 will create a thermal lens resulting in severe phase distortion of the propagating beam [26]. The thermal nonlinearity of n_2 is related with the thermo-optic coefficient $\left(\frac{dn}{dT}\right)$ by the formula of $\left[\left(\frac{dn}{dT}\right) = \frac{4\, n_2\, \kappa}{\alpha_0\, \omega_0^2}\right]$ where κ=0.129 *(W/m K)* is the thermal conductivity of the solvent. The two values of the $\left(\frac{dn}{dT}\right)$ of the 1,1′-(Ethylene-1,2-diyl)dipyridinium dichlorodinitratocuprate(II) are tabulated in Table 4.

3.2. Figures of merit "FOM"

To check the suitability of our sample for photonic devices, it should satisfy many requirements, such as: large Kerr nonlinearity, low linear and nonlinear losses and ultrafast response time. These requirements are expressed in two equations 2 and 3:

$$W = n_2 I / \alpha_0 \lambda \quad (2)$$

where "I" is the incident light intensity.

$$T = \beta \lambda / n_2 \quad (3)$$

According to the literature [21], the values of W (one photon) and T (two-photon) should have the characterization as: $W >> 1$ and $T << 1$. Our calculated results of *W* and *T* are tabulated in Table 5, which satisfy the two previous conditions (equations 2 and 3) for all optical switching. So, we suggest that the 1,1′-(Ethylene-1,2-diyl)dipyridinium dichlorodinitratocuprate(II) is considered to be used in a future photonic applications.

Table 4. The linear absorption coefficient, linear refractive index, σ_g, σ_{ex} and thermal-optic coefficient $(\frac{dn}{dT})$ parameters of of $[C_{12}H_{14}N_2][CuCl_2(NO_3)_2]$. in DMSO with concentration of 10^{-3}M.

Wave-lengths	$\alpha_0(cm^{-1})$	n_0	$\sigma_{opt}(s^{-1})$	$\sigma_e(\Omega cm^{-1})$	$\left(\frac{dn}{dT}\right)(1/k)$	σ_g (cm^2)	σ_{ex} (cm^2)
λ= 635 nm	**0.534**	**1.327**	**1.6×10^{9}**	**3.8×10^{5}**	**5.04×10^{-4}**	**8.87×10^{-19}**	**4.19×10^{-14}**
λ= 532 nm	**0.453**	**1.327**	**1.4×10^{9}**	**3.3×10^{5}**	**1.37×10^{-4}**	**7.52×10^{-19}**	**1.11×10^{-13}**

Table 5. The calculated nonlinear parameters of 1,1'-(Ethylene-1,2-diyl)dipyridinium dichlorodinitratocuprate(II) with concentration of 10^{-3}M

Wave-lengths	n_2 (cm^2/W)	β (cm/W)	Re (χ^3) (esu)	Im(χ^3) (esu)	F.O.M	
					W	T
λ= 635nm	5.32×10^{-8}	3.59×10^{-4}	2.95×10^{-6}	1.03×10^{-5}	1.57	0.43
λ= 532nm	8.61×10^{-8}	5.71×10^{-4}	4.78×10^{-6}	1.34×10^{-5}	5.09	0.36

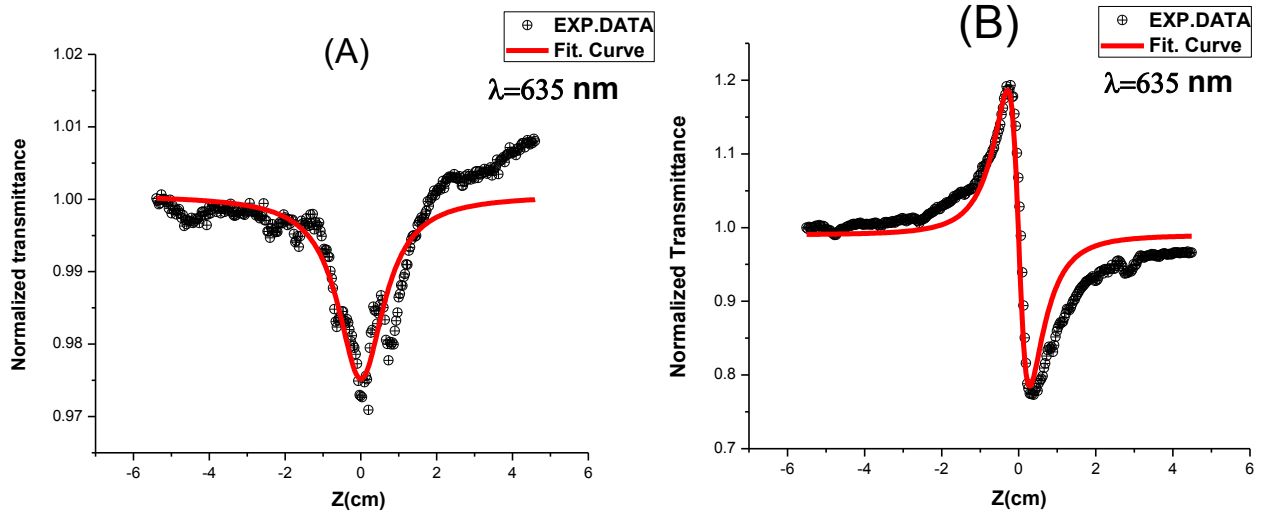

Fig. 6. (a) Open aperture and (B) closed aperture z-scan measurements of 1,1′-(Ethylene-1,2-diyl)dipyridinium dichlorodinitratocuprate(II) in DMSO with concentration of 10^{-3}M, at λ= 635nm. The solid line is a fit of the experimental data (color online)

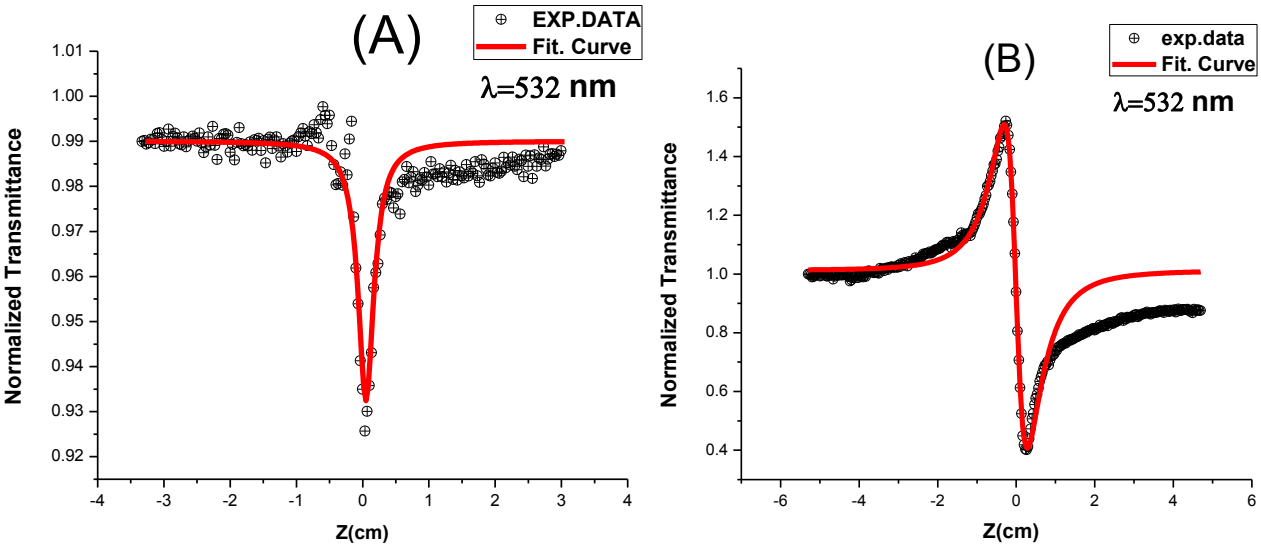

Fig. 7. Normalized transmittance (close aperture) of 1,1′-(Ethylene-1,2-diyl)dipyridinium dichlorodinitratocuprate(II) in DMSO with concentration of 10^{-3}M at two laser wavelengths, λ= 635 and λ= 532 nm. The solid line is a fit of the experimental data (color online)

3.3. All optical switching

The Z-scan with pump-probe beams configuration was used to observe optical switching behavior. Both, the pump and the probe beams were focused on the sample by the same lens. The pump beam (Power of 40 mW) was modulated with mechanical chopper at frequency of 60 Hz. A brief description is given as follows: the mechanism of optical switching which is based on linear and nonlinear absorption, When the probe laser beam propagates through the nonlinear medium (sample); the output intensity is in the switch-on states due to the higher linear transmittance. When, the sample is pumped by a strong laser beam; the nonlinear effect dominates, so that output intensity would be switched off [13, 27]. Full details of the optical switching mechanism were given in ref [12]. Fig. 8 shows an oscilloscope trace (probe) of transient optical switching (below) together with the modulated pump signal (above). The measured switch on time was less than 10 ms using modulated input pump beam.

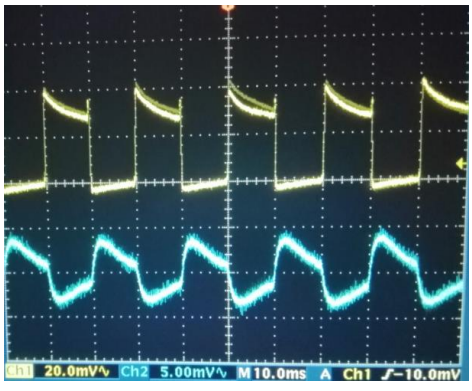

Fig. 8. Optical switching effect: pump beam (upper trace) and probe beam (lower trace) (color online)

Our reported results for n_2 and β of 1,1′-(Ethylene-1,2-diyl)dipyridinium dichlorodinitratocuprate(II) can be compared with other studied molecules under the same experimental conditions [12-13, 28].

Extra experiment was carried out to clarify that the pure solvent sample has no contribution to the recorded data during the two cases (opened /closed scan).

4. Conclusions

A new organic-inorganic hybrid salt: 1,1′-(Ethylene-1,2-diyl)dipyridinium dichlorodinitratocuprate(II) was prepared , spectroscopic characterized and the NLO properties were investigated. The values of α_0, n_0, n_2, β, Re χ^3, Imχ^3 and the thermo-optic coefficient were estimated using Single beam z-scan configuration at two wavelengths, λ= 532 nm and λ= 635 nm. It was found that all the NLO coefficients at λ= 532 nm are better when using laser wavelength at λ= 635 nm. Also, the optical switching in the 1,1′-(Ethylene-1,2-diyl)dipyridinium dichlorodinitratocuprate(II) was observed utilizing the z-scan with pump-probe beams.

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