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Synthesis, characterization and third-order optical non-linearity of the 1,1′-(Ethylene-1,2-diyl)dipyridinium tetranitratocuprate(II)

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The new 1,1'-(Ethylene-1,2-diyl)dipyridinium tetranitratocuprate(II) was synthesized and characterized using different spectroscopic methods. The nonlinear optical properties have been investigated by z-scan technique. Theoretical fit to the experimental data was carried out to evaluate the nonlinear absorption coefficient (β), the nonlinear negative refractive index (n_2), the ground-state absorption cross sections (σ_g), the excited-state absorption cross sections (σ_{ex}) and thermo-optic coefficient. The obtained results suggest that our complex is considered to be good candidate for future optoelectronic devices.

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1. Introduction

Organometallic materials were found to have large third-order nonlinear optical susceptibility. Such valuable feature has encouraged the researchers to use the organometallic complexes in the field of optoelectronic devices [1- 6]. In organometallic complexes, the NLO-effects are most probably due to the conjugation of d orbital electrons (transition metal centers) and delocalized π–electrons (coordinated organic ligands). Furthermore, the ease in chemical alteration and reduction in cost, placing them as: interesting materials for comparison with the typical inorganic NLO crystals [7].

A lot of works have been done on the transition metal complexes to study their nonlinear optical properties [8-15]. More specifically, the nonlinear optical properties of copper complexes have been investigated by many research groups [16-18]. They found that these complexes have been exhibiting high nonlinear optical response.

The z-scan technique [19-20] is used to estimate both the nonlinear absorption (NLA) and the nonlinear refractive index (NLR) for different molecules. The nonlinear optical effects arise due to the changes of the refractive index and absorption coefficient during the interaction between the strong laser intensity and the studied molecules.

Since, we are interested in expanding the hybrid salts of 1,1′-(Ethylene-1,2-diyl)dipyridinium $[C_{12}H_{14}N_2]^{2+}$ to include nitrato-derivatives, we report the third order nonlinear optical properties of the 1,1′-(Ethylene-1,2-diyl)dipyridinium tetranitratocuprate(II) solution using z-scan technique with a CW diode laser radiation at 635 nm. There are no reports available on the literature, regarding the NLO properties of such compound. The objective of this work is to evaluate the figures of merit of the nonlinear optical coefficients of the copper complex.

2. Experimental techniques

2.1. Materials and methods

All procedures were conducted in air with reagent grade solvents. $AgNO_3$ (PROLABO, EEC) and $Cu(NO_3)_2.3H_2O$ (BDH, Germany) were commercial samples and used as received. $[C_{12}H_{14}N_2]Br_2$ was prepared as described previously [21-22].

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a *Bruker Bio spin 400* spectrometer (Switzerland). Fourier transform Infrared (FTIR) spectrum was recorded on *Thermo-Nicolet 6700* FTIR Spectrometer, taken as KBr disc with a resolution of 4 cm^{-1}. Microanalysis was performed using *EURO EA* (Italy). The Ultra-Violet-Visible (UV-Vis) absorption spectrum was recorded in the wavelength range 190-1100 nm using UV-1601 PC Shimadzu Spectrophotometer.

2.1. 1. Synthesis of 1,1`-(ethylene-1,2-iyl) dipyridinium dinitrate monohydrate

To an aqueous solution of 0.40 g (1.16 mmol) $[C_{12}H_{14}N_2]Br_2$ in H_2O (3 ml) was added drop wise to a solution of 0.40 g (2.37 mmol) $AgNO_3$ in H_2O (3 ml) with rapid stirring at ambient temperature. The resulting mixture was stirred for 3 h and then filtered to get rid of AgBr, solvent was removed *in vacuum* to afford quantitatively product $[C_{12}H_{14}N_2](NO_3)_2{\cdot}H_2O$, which was washed with EtOH to afford white powder (268 mg, yield 70%).

2.1.2. Synthesis of 1,1`-(ethylene-1,2-iyl) dipyridinium tetranitratocuprate(II)

A solution of 0.20 g (0.60 mmol) $[C_{12}H_{14}N_2](NO_3)_2{\cdot}H_2O$ in H_2O (3 ml) was added to a solution of 0.145 g (0.60 mmol) $Cu(NO_3)_2.3H_2O$ in H_2O (3 ml), the resulting solution was heated to 60 °C overnight. The solvent was then removed *in vacuum* to afford quantitatively product *(II)*, which was washed with EtOH to afford sky blue powder (180 mg, yield 60%).

2.2. Z-scan measurements

To investigate the third order nonlinear optical properties of the 1,1′-(Ethylene-1,2-diyl)dipyridinium tetranitratocuprate(II), the z-scan technique was used. A linearly polarized TEM_{00} Gaussian beam a diode laser was used as the light source. The laser model is **CUBE™** Diode Laser System, Coherent-635-3QE, λ= 635nm; the power is up to 26 mW. The z-scan measurements in open /closed aperture configurations were carried out for input intensity of I_0= 1026 W/cm^2. The experimental setup will not be presented in full detail, all the information can be found in our previous work [23]. The samples were prepared by an accurately weighed amount of the 1,1′-(Ethylene-1,2-diyl)dipyridinium tetranitratocuprate(II) and dissolving it in DMSO to obtain samples of two concentrations of $2.6{\times}10^{-3}$M and 10^{-3}M.

3. Results and discussion

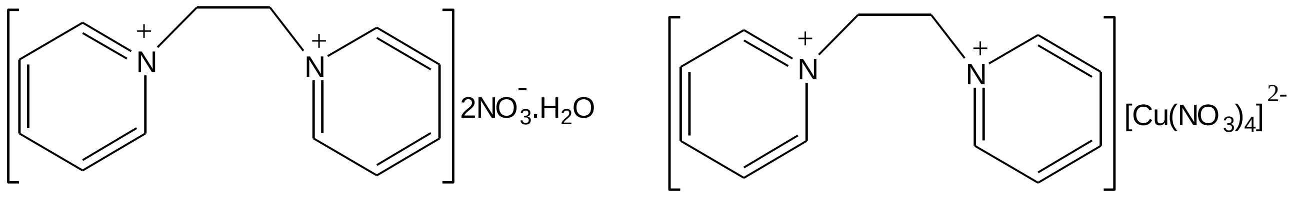
3.1. Spectroscopic characterizations

The available salt $[C_{12}H_{14}N_2]Br_2$ was readily converted into 1,1`-(ethylene-1,2-diyl)dipyridinium dinitrate monohydrate $[C_{12}H_{14}N_2](NO_3)_2{\cdot}H_2O$ (I) by substitution reaction utilizing $AgNO_3$. The new blue hybrid salt $[C_{12}H_{14}N_2][Cu(NO_3)_4]$ (II) was obtained by treatment of (I) with $Cu(NO_3)_2$ in an a aqueous solution. Both products (I) and (II) were purely isolated salts and characterized by multinuclear NMR, FTIR, and UV-vis spectroscopies and elemental analyses. The obtained compounds (I) and (II) are both water soluble, each one is highly insoluble in common organic solvents, but each one has a good solubility in dimethyl sulfoxide (DMSO). Their composition and properties are summarized in Table 1.

Since the dication $[C_{12}H_{14}N_2]^{2+}$ is the same for both (I) and (II) (Fig. 1), as expected their ^{1}H and ^{13}C{^{1}H} NMR spectra are very similar and have the same features to their corresponding ones of the parent salt $[C_{12}H_{14}N_2]Br_2$ [19]. The ^{1}H and ^{13}C{^{1}H} NMR spectra of (I) and (II), each showed the expected four resonances for four different proton environments and four singlets for four environmentally different C centres respectively. The ^{1}H and ^{13}C{^{1}H}NMR spectra of II (DMSO, 25°C) are shown in Figs. 2 and 3, and the NMR spectroscopic data for I and II are depicted in Table 2.

Noteworthy, although the two experimental FTIR spectra of I and II are fairly similar, but that of II has a distinctive absorption band at 506 cm^{-1} (Fig. 4), this finger print region band is very informative and readily attributed to the symmetric stretching mode of the Cu–O bond in complex II [24-25]. Moreover, the FTIR spectrum of complex (I) has also a characteristic absorption band at 1583 cm^{-1}, which is consistent with bending vibration for H_2O molecules of (I) [26].

The UV-Vis spectrum of II is shown in Fig. 5, which was recorded using UV-3101PC Shimadzu. The absorption band at λ_{max}= 260 nm is due to the combination of π–π^* and intraligand charge-transfer (ILCT) transitions [5]. The weak broad spectral feature, which can be distinguished in the spectrum in the range 300–340 nm is more likely to be associated with the (d→d*) transition and/or ligand-to-metal charge-transfer (LMCT) in the inorganic part $[Cu(NO_3)_4]^{2-}$ of the complex.



I

II

Fig. 1 Molecular structures of complexes I and II

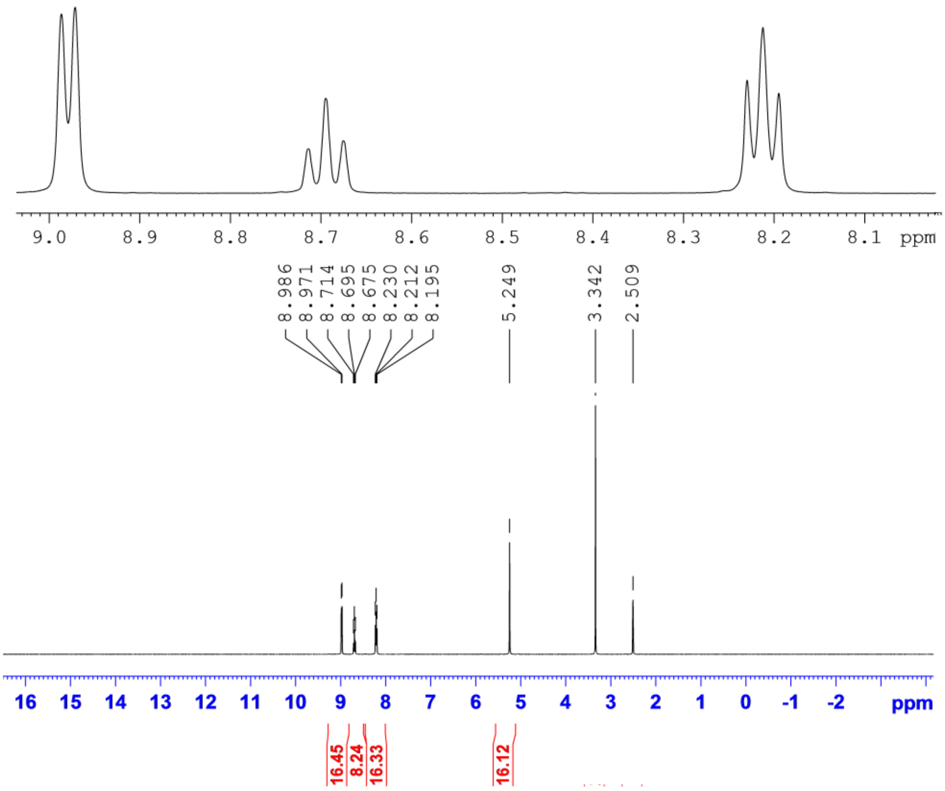


Fig. 2. ^{1}*H NMR spectrum of complex II (DMSO, 25°C).*

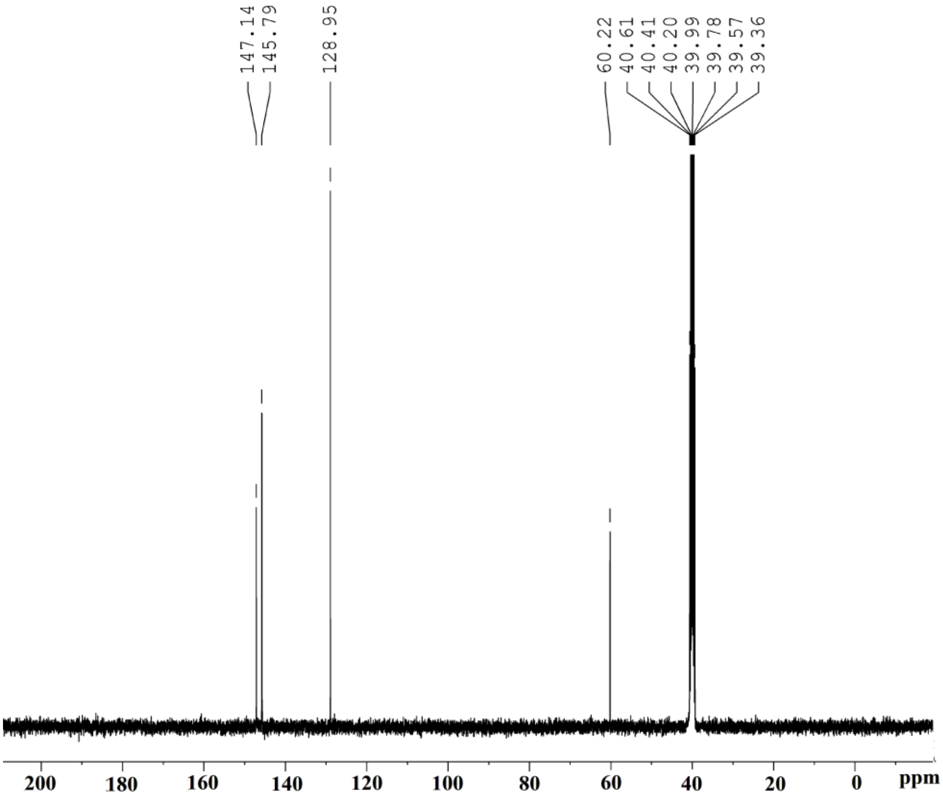


Fig. 3. ^{13}*C{*^{1}*H} NMR spectrum of complex II (DMSO, 25°C).*

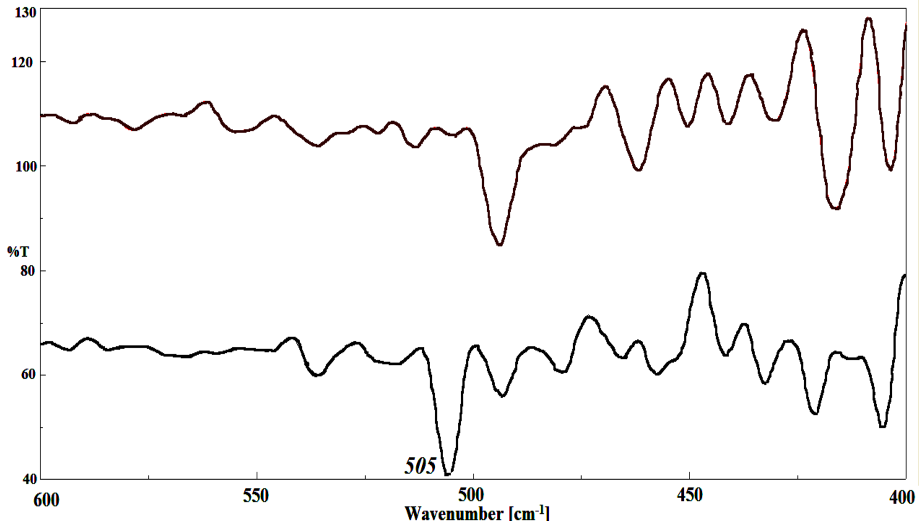


Fig. 4. Experimental FTIR spectra of complexes I (top) and II (bottom) in the range of 400-600 cm^{-1}.

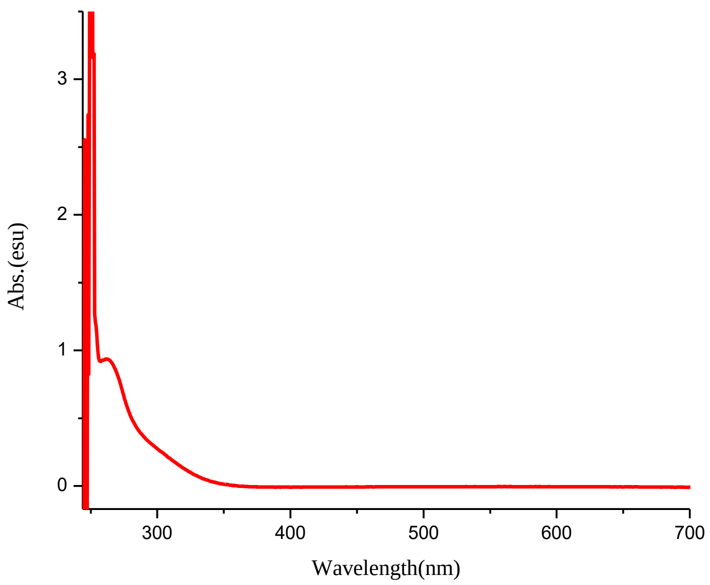


Fig. 5 UV-Vis spectrum of complex II at concentration of 10^{-4} M.

3.2. Nonlinear optical investigation

The nonlinear optical coefficients n_2 and β of complex (II) were evaluated using z-scan experiments. Fig. 6 shows the open aperture (OA) scan of the complex in DMSO with concentrations of 2.6×10^{-3}M and 1×10^{-3}M. When the sample is moved through the focal point at z =0 of the laser radiation, the total transmission curve is symmetric with respect to focus (z=0).

The value of the 3rd nonlinear absorption coefficient (β) was estimated from the fits of the experimental data of OA using the following equation [13]:

$$T(z) = 1 - \frac{(I_0 L_{eff} \beta)}{[2^{\frac{3}{2}}(1 + \frac{z^2}{z_0^2})]} \quad (1)$$

where L_{eff} = (1- exp (-α_0L))/α_0 is the effective thickness of the sample, L is the thickness of the sample, α_0 is the linear absorption coefficient, $z_0 = \pi\omega^2{}_0/\lambda$ is diffraction length of the beam, λ is the laser wavelength, and I_0 is the laser intensity at z = 0. The symbols present the experimental data, while the "solid lines" is the fitting curves.

The shape of the curves (Fig. 6) suggest that the complex exhibited a reverse saturable absorption (RSA) processes, these features can be confirmed by comparing the magnitude of the values of cross-sections of the ground state (σ_g) and the excited state (σ_{ex}), where $\sigma_{ex} >> \sigma_g$. These NL processes were explained on the basis of the five-level model in organic compounds with extended π- electron system [27-30]. The nonlinear absorption coefficient β depends on the absorption cross-section of ground and excited states as given by equation, 2 [13]:

$$\beta = \frac{\lambda N_0 \Delta\sigma}{4\pi I_s} \tag{2}$$

where $\Delta\sigma = \sigma_{ex} - \sigma_g$, N_0 is the total concentration in cubic unit (cm^3), and $I_s = \frac{hc}{\lambda \sigma_g \tau}$, where $\frac{hc}{\lambda}$ is the pump-photon energy, τ is the excited lifetime and taken to be 1ms (triplet state decay time). The ground-state absorption cross section was calculated from $\sigma_g = \alpha_0 / N_0$. Using Equation (2), the excited-state absorption cross sections was calculated at 635 nm. Both, values of the σ_{ex} and the σ_g were listed in Table 3. The σ_{ex} is nearly (four times) higher than the σ_g, this confirms that the nonlinear absorption here is from RSA processes.

The closed aperture (CA) measurements lead to evaluate the nonlinear refractive index (n_2), a small aperture was located in front of the detector. Since, the closed aperture transmittance is mix of the nonlinear refraction and nonlinear absorption components. The division method [27] was used to eliminate the nonlinear absorption component effect. Fig. 7 shows the data of the CA/OA scan (the symbols) of complex (II) in DMSO at two concentrations of 2.6×10^{-3}M and 10^{-3}M. While the fitting curves were obtained using equation 3 [19-20]:

$$T(z, \Delta\phi) = 1 - \frac{4\,\Delta\phi_0\; X}{(X^2 + 9)\,(X^2 + 1)} \tag{3}$$

where is $X = (Z/Z_0)$, and T is the normalized transmittance for the pure refractive nonlinearity, and $\Delta\phi_0$ is the on–axis nonlinear phase shift. Then the value of $\Delta\phi_0$ can be inserted in the formula $[n_2 = \frac{\lambda \Delta\phi_0}{2\pi I_0 L_{eff}}]$ to calculate the nonlinear refractive index n_2.

The real and imaginary parts of the third-order nonlinear optical susceptibility $|\chi^3| = [Re(\chi^3)^2 + Im(\chi^3)^2]^{1/2}$ can be determined by calculating of the n_2 and β with the same method described in [13]. The values of α_0 and n_0 were determined by similar method in reference [23] and listed in Table 3. Also, the values of n_2, β, $|Re\ \chi^3|$ and $|Im\ \chi^3|$ are given in Table 4.

The shape of the curves (Fig. 7) have a peak-valley configuration, which gives a direct indication of negative n_2 and the sample can be considered as self-defocusing material around λ= 635nm. The defocusing effect obtained in our sample is due to thermal nonlinearity rising from absorption of a focused CW laser beam propagating through an absorbing medium producing a spatial distribution of temperature in the solution. The spatial variation of the refractive index will act as a thermal lens resulting in severe phase distortion of the propagating beam [31-34].

Concentration effect is very clear in both Figures 6 and 7, the values of β and n_2 increase with increasing in concentration and this is attributed to the increase in number of molecules. With more concentrated solution additional particles get thermally agitated, resulting in enhanced nonlinear absorption [27, 33].

The two figures of merit, "FOM" $W = n_2 I / \alpha_0 \lambda$ and $T = \beta\lambda / n_2$ have been calculated to clarify the suitability of II for photonic devices. According to the literature [7] the values of W (one photon) and T (two-photon) have the characteristic as: $W > 1$ and $T < 1$. The values of W and T are listed in Table 4. That confirms complex (II) is suitable to be used for the optical applications.

As CW laser is used as excitation source, the observed optical nonlinearity of the samples is a thermal origin, arising from the temperature dependence of the refractive index. The thermal nonlinearity (n_2) is related with the thermo-optic coefficient $\left(\frac{dn}{dT}\right)$ by the following formula $[\left(\frac{dn}{dT}\right) = \frac{4\, n_2\, \kappa}{\alpha_0\, \omega_0^2}]$ where κ = 0.1567 *(W/m K)* is the thermal conductivity of the solvent. The obtained values of the thermo-optic coefficient of II are listed in Table 3.

It is well established that the NLO response of complex II may come from a structure factor [35]. And it has been suggested that these kind of complexes show improved optical nonlinearities due to their expanded π-electron system and the presence of the heavy central metal [36-38]. Furthermore, complex II shows large third – order nonlinear optical properties due to the delocalized electronic states formed by π→π* and d→d* transitions [7]. Indicating that this type of molecules are promising NLO materials.

Our reported values of n_2 and β for II (Table 4) can be compared with the recently reported values in literature for molecules with CW laser excitation [12-13, 32, 35].

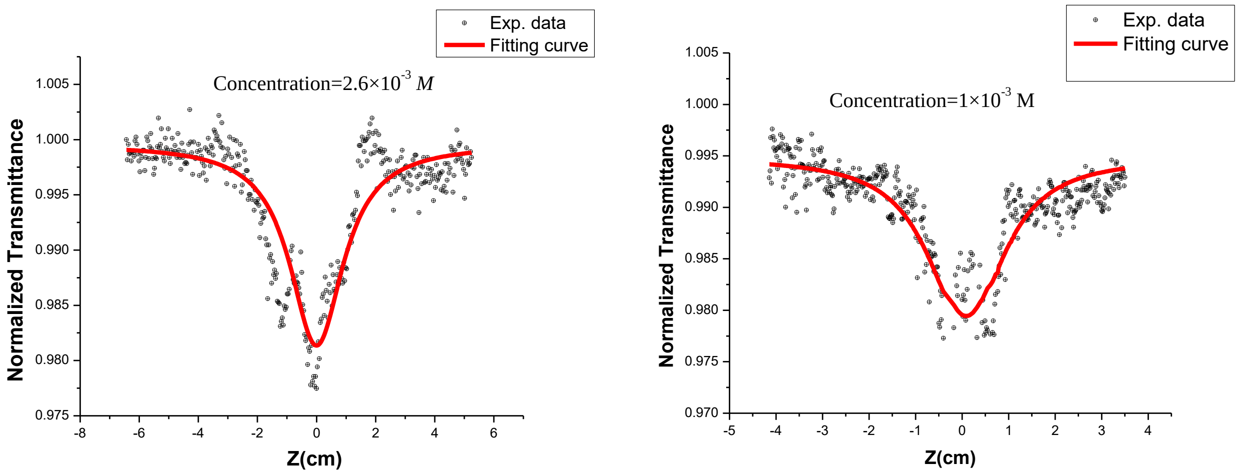


Fig. 6. Open aperture z-scan data of complex II in DMSO at two concentrations of 2.6×10^{-3} M and 1×10^{-3} M

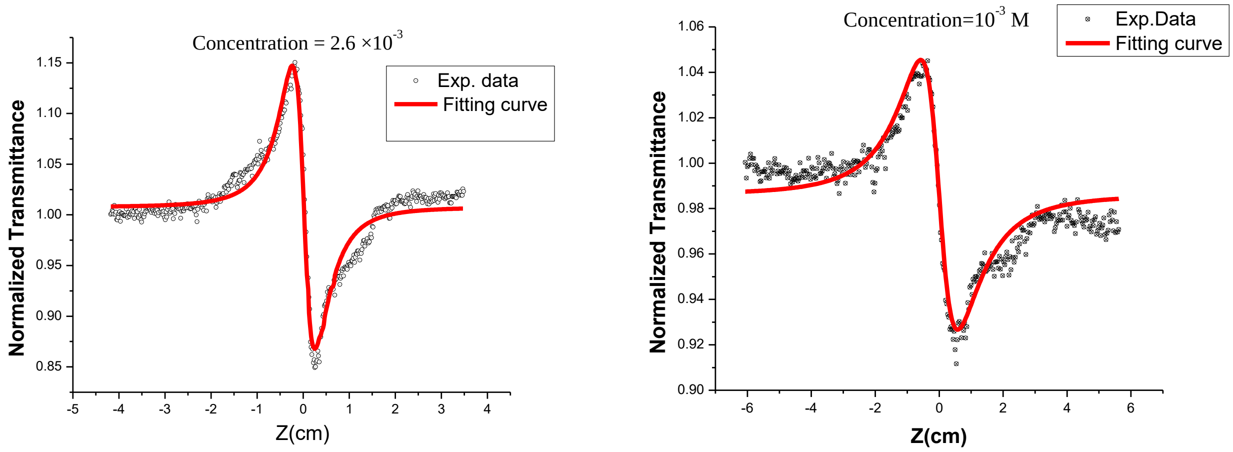


Fig. 7. Pure (C/O aperture) z-scan data of complex II in DMSO at two concentrations of 2.6×10^{-3} M and 1×10^{-3} M

Finally, the same z-scan measurements were applied to a pure solvent sample (DMSO) to find out its contribution, but no signals were observed in either the opened or the closed z-scan configurations.

Table 1. Characterization data for complexes I and II

Compound	Formula	M.W.	w_i(calc.) /%	w_i(found) /%	Yield (%)	M.P. (°C)
I White powder	$C_{12}H_{16}N_4O_7$	328.28	C: 43.90 H: 4.91 N: 17.07	C: 43.24 H: 4.09 N: 18.36	70	212
II Sky blue powder	$C_{12}H_{14}N_6O_{12}Cu$	497.82	C: 28.95 H: 2.83 N: 16.88	C: 28.96 H: 1.91 N: 18.17	60	179

Table 2. Spectral data of complexes I and II

Compound	Spectral data
I	^{1}H NMR (DMSO-d_6), δ 5.26 (s, 4H, CH_2), 8.21 (m, 4H, py), 8.69 (m, 2H, py), 8.99 (m, 4H, py) ^{13}C{^{1}H}NMR (DMSO-d_6), δ 60.21 (CH_2), 128.94 (Py), 145.80 (Py), 147.13 (Py) IR (KBr) ν cm^{-1}: 1583.2 (H-O), 1384.68 (NO_3).
II	^{1}H NMR (DMSO-d_6), δ 5.22 (s, 2H, CH_2), 8.19 (m, 4H, py), 8.67 (m, 2H, py), 8.95 (m, 4H, py). ^{13}C{^{1}H} NMR (DMSO-d_6), δ 60..20 (CH_2), 128.93 (Py), 145.77 (Py), 147.12 (Py). IR (KBr) ν cm^{-1}: 506.2 (Cu-O), 1384.64 (NO_3). UV(H_2O): λ max (ε) = 218.0 (1.014), 257.5 (0.642).

Table 3. The linear absorption coefficient, linear refractive index, σ_g, σ_{ex} and thermal-optic coefficient $(\frac{dn}{dT})$ parameters of complex (II) in DMSO with concentrations of 2.6×10^{-3} M and 1×10^{-3} M

Sample concentrations	α_0 (cm^{-1})	n_0	$(\frac{dn}{dT})\times10^{-5}$ $(1/k)$	σ_g (cm^2)	σ_{ex} (cm^2)
2.6×10^{-3} *M*	0.741	1.469	2.17	4.73×10^{-19}	1.02×10^{-14}
1$\times10^{-3}$ *M*	0.653	1.470	1.49	1.08×10^{-18}	2.37×10^{-14}

Table 4. The calculated nonlinear of complex (II) in DMSO with concentrations of 2.6×10^{-3}M and 1×10^{-3}M

Sample concentrations	n_2 (cm^2/W)	β (cm/W)	Re ($\chi^{□}$) (esu)	Im($\chi^{□}$) (esu)	FOM	
					W	T
2.6×10^{-3}	2.11×10^{-8}	1.23×10^{-4}	1.15×10^{-6}	3.40×10^{-6}	1.46	0.37
1×10^{-3}	1.54×10^{-8}	2.51×10^{-4}	8.44×10^{-7}	6.69×10^{-6}	1.03	0.38

4. Conclusions

In summary, the organic-inorganic hybrid salt $[C_{12}H_{14}N_2](Cu(NO_3)_4]$ was synthesized and characterized. The z-scan method using a CW diode Laser (λ= 635 nm) was used to calculate the values of α_0, n_0, n_2, β, Re χ^3, Imχ^3 and the thermo-optic coefficient. Expectedly, the complex exhibits large NLO response due to the association of the aromatic π-electron system of $[C_{12}H_{14}N_2]^{2+}$ and partially filled d electron set of ion centre (Cu^{2+}). The obtained results also exhibit the complex producing self-defocusing property with negative value of n_2.

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