# Nonlinear optical investigation of molybdenum phenanthroline complex

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A new molybdenum phenanthroline complex was synthesized and characterized using different spectroscopic methods. The nonlinear optical properties have been investigated (refraction and absorption) by z-scan technique with a CW diode laser radiation (λ=635nm, 26 mW). Theoretical fit of the experimental data was carried out to evaluate the third order nonlinear optical parameters and the thermo-optic coefficient. The observed results show that, the proposed complex could be considered as a good candidate for future optoelectronic devices and applications.

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## 1. Introduction

Organometallic materials with large nonlinear optical response have attracted considerable attention due to their uses in photonic applications [1-8]. The advantages of these organometallic materials over inorganic NLO crystals are based on their simple processes of chemical synthesis as well as low cost giving them the potential to be good competitive materials for optical applications [9].

The origin of the nonlinear optical effect in the organometallic materials is due to the interaction between "d" electrons of the transition metal atom and the conjugated bonds existing in organic ligand with π–electron [10].

Recently, more researchers have concentrated their work on metal complexes for their nonlinear optical properties [10-18]. More specifically, molybdenum carbonyl complexes with organic ligands are exhibiting biological and optical properties. These complexes exhibit photochemistry, photo-activation and biological properties; due to their bidentate N-N coordination bound ligands and the charge transfer in the complex. This leads to enhance the nonlinear optical characteristics in the visible range of the electromagnetic radiation [19-20].

The z-scan method [21-22] is an effective and simple setup for estimating the nonlinear optical parameters, such as the nonlinear optical refractive index ($n_2$) and the nonlinear optical absorption (β). In addition to that, theoretical calculations were carried out in order to estimate the nonlinear optical parameters, as well as to estimate the figures of merit of nonlinear materials. This paper reports about the synthesis, characterization and third order nonlinear optical properties including the efficiency of calculated nonlinear coefficients parameters of molybdenum phenanthroline complex in solution by employing z-scan technique with a CW laser (λ=635nm).

## 2. Experimental techniques

### 2.1. Materials and methods

All starting chemical materials were used as received for the synthesis of molybdenum phenanthroline complex without any further purification. A 0.015 L of absolute ethanol from Prolabo was placed in round dried flask (250 mL), bubbled with nitrogen gas (99.999 %) for about fifteen minutes for removing any existing oxygen gas, then, 1.2 mmole of molybdenum hexacarbonyl from Fluka, 2.5 mmole of 1,10-phenanthroline (from Serva) and 2.6 mmole of sodium borohydride (from Avochem) were added directly into the round flask and then connected to vacuum line system. The flask containing the previous mentioned mixture was evacuated until the ethanol boiling, and then nitrogen gas was inserted to the system. This

procedure was repeated five times in order to be sure for getting rid of any remaining oxygen in the system. Then, the flask containing the reacting mixture was heated in an oil bath at 80°C under refluxing for about four hours. The resulted material was in dark red viscose form. The material was purified three times by dissolving it in methyl ethyl ether and filtered, then, the solvent was removed from the material under vacuum and the final objective obtained complex of molybdenum phenanthroline was kept in dark under nitrogen atmosphere for analysis and further investigation. The proposed structure of the synthesized molybdenum phenanthroline complex, MPTC is depicted in Fig. 1.

### 2.2. Z-scan measurements

The experimental setup was explained in full detail in our previous work [23]. The used laser model is **CUBE™** Diode Laser System, Coherent-635-30QE, special optical filter was inserted in front of the laser beam to get $TEM_{00}$ Gaussian beam, $\lambda$= 635nm; the power is up to 26 mW. The z-scan measurements in an open aperture/closed aperture configurations were carried out with the input intensity of $I_0$=1334 W/cm$^2$. The studied samples were prepared by an accurately weight amount of the MPTC dissolved in chloroform with two different concentrations at $10^{-3}M$ and $10^{-4}M$.

### 2.3 UV-Vis and FTIR characterizations

The UV-Vis absorption spectrum of the synthesized MPTC Complex was taken in the chloroform solution, which has been used as reference. The spectrum was recorded in the wavelength range 190 nm – 700 nm using UV-1601 PC Shimadzu Spectrophotometer. The UV-Vis spectrum of MPTC (Fig. 2) shows two absorption peaks around 340 nm and 373 nm. Both transitions can be assigned mainly to $\pi \rightarrow {}^*\pi$ and
$d \rightarrow {}^*d$ transitions in the complex, respectively. The optical properties of these complexes exclusively results in substitution reactions of an axial CO ligand. The carbonyl substitution in the ground state of $[Mo(CO)_2(N\text{-}N)_2]$ has associative character enhancing the metal-to-ligand charge transfer factor in the prepared complex [24].

The Fourier transform infrared spectrum (FTIR) of MPTC was recorded at room temperature. Fig. 3 shows the recorded infrared spectrum as KBr disc and scanned in the range 400-4000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$ and 64 scans as direct measurements using Nicolet 6700 spectrometer instrument (Thermo Nicolet, USA). The operating software used system was OMNIC software (Version 7.3, Thermo Nicolet, USA). A background spectrum of air as reference was scanned prior to any measurements. The Fourier transforms infrared spectrum (Fig. 3) shows three characteristic vibrational bands for the CO ligands at 2008, 1894 and 1870 cm$^{-1}$. The band at 2008 cm$^{-}$1 can be assigned to the axial carbonyl ligands due to the strong *trans*-effect by $\pi$- acceptor ability of the ligands. The two bands at 1870 and 1894 cm$^{-1}$ are assigned to the symmetric and antisymmetric vibrations of the equatorial carbonyl group respectively. This observation is consistent with earlier report work in the literature [25-27]. Finally the whole remaining bands in the spectrum are due to phenanthroline bounded vibrational frequencies.

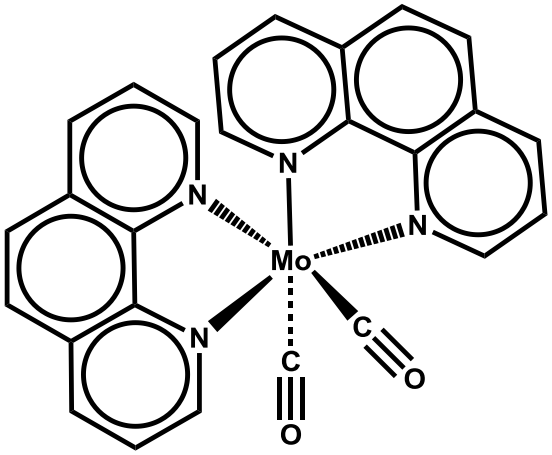


*Fig. 1 Molecular Structures of $Mo(CO)_2(Phen)_2$ [MPTC]*

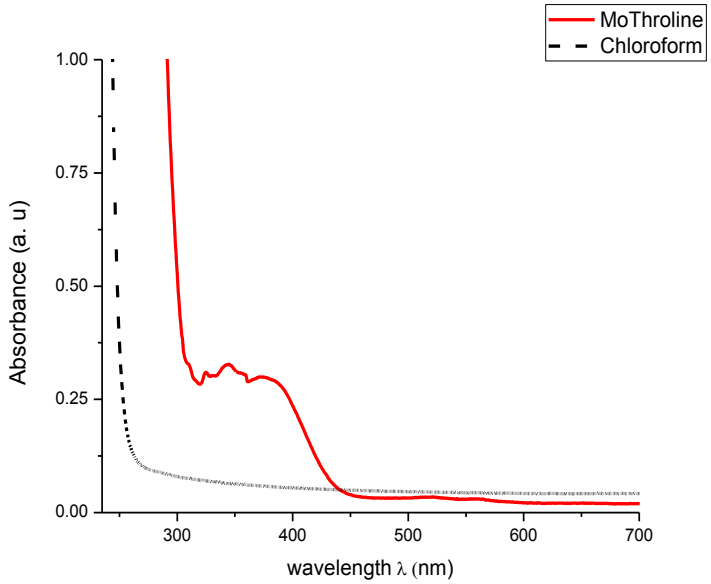


*Fig. 2 UV-Vis spectrum of MPTC solution at concentration of $10^{-4}$ M (color online)*

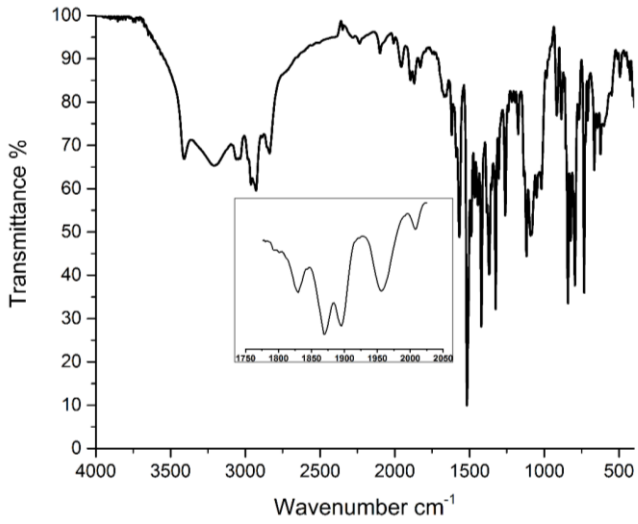


*Fig. 3 FTIR spectrum of MPTC as KB disc*

## 3. Results and discussion

In the present study, the z-scan measurements were employed to estimate the nonlinear optical coefficients $n_2$ and β of the MPTC in chloroform at two different concentrations at $10^{-3}$M and $10^{-4}$M. Fig. 4 shows the open aperture scan of MPTC in chloroform, this curve exhibited normalized transmittance valley. The shape of the curve is symmetrical with respect to focal point (z=0), this indicates to the presence of NLO absorption.

The nonlinear absorption coefficient (β) is determined by fitting the experimental data of open aperture (OA) to eq. 1 [15]:

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

Here, $L_{eff} = (1- \exp(-\alpha_0 L))/\alpha_0$ is the effective thickness of the sample, L is the thickness of the sample, $\alpha_0$ is the linear absorption coefficient (calculated using Beer-Lambert Law), $z_0 = \pi\omega^2_0/\lambda$ is diffraction length of the beam, **λ** is the laser wavelength, and $I_0$ is the laser intensity

at z=0. In Fig. 4, the symbols present the experimental data, while the "solid lines" is the fitting curves.

The curves (Fig. 4) suggest that the MPTC exhibited a reverse saturable absorption (RSA) mechanism, this can be confirmed when the $\sigma_{ex} >> \sigma_g$ , where is $\sigma_g = \alpha_0/N_0$ cross-sections of the ground state ($N_0$ is the total concentration of the samples in a cubic unit ( $cm^3$ ) and $\sigma_{ex}$ is the excited state. However, RSA mechanism was explained in full details depending on the five-level model in organic compounds with extended π- electron system [28-31]. We have calculated the $\sigma_{ex}$ and $\sigma_g$ at λ=635 nm, according to our previous work [15] and listed in Table 1. The present results are shown that, the $\sigma_{ex}$ is five times more than the $\sigma_g$.

We have studied the relation between the excitation intensity ($I_0 = 2p / \pi\omega^2_0$, where P is the power of the laser beam) and the evaluated of the NLA coefficient β (Fig. 5). The NLA coefficient β decreases gradually with increasing excitation intensity, that is a consequence of sequential two-photon absorption and Excited state absorption (ESA) assisted RSA process [32- 33].

The closed-aperture (CA) setup helps to determine the nonlinear refractive index $n_2$, (usually, a small aperture is located in front of the detector). Also, the closed aperture data is mixed from two components: β and $n_2$. We used the division method [28] to eliminate the effect of β. Our results (Fig. 6) show the pure experimental data of the CA/OA scan (the symbols) of the MPTC sample in chloroform at two different concentrations of $10^{-3}M$ and $10^{-4}M$. The fitting curves were obtained using eq. 2 [21-22]:

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

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

The real and imaginary parts of the third-order nonlinear susceptibility $|\chi^3| = [\mathrm{Re}(\chi^3)^2 + \mathrm{Im}(\chi^3)^2]^{1/2}$ can be determined by calculating the $n_2$ and β with the same method described before [15]. The values of $\alpha_0$ and $n_0$ were determined by similar [23] and listed in Table 1. Also, the values of $n_2$, β, $|\mathrm{Re}\ \chi^3|$ and $|\mathrm{Im}\ \chi^3|$ are given in Table 2.

The closed-aperture curves (Fig. 6) have peak-valley shape, indicating to the negative value of $n_2$. This let to consider our sample as self-defocusing material at 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 [34-37].

Our results show that the existing of concentration effect on the values of β and $n_2$ (Figs. 4 and 6), it seems to be the values of β and $n_2$ increase with concentration increasing as resulting of the increase in number of molecules interaction and collision leading to enhance nonlinear absorption effect [28, 36].

As we used CW laser in our work, the optical nonlinearity of the studied samples is due to thermal origin, which comes 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 [19]:

$$\left[\left(\frac{dn}{dT}\right) = \frac{4\,n_2\,\kappa}{\alpha_0\,\omega_0^2}\right] \qquad (3)$$

where κ=0.129 *(W/m K)* is the thermal conductivity of the solvent. The values of the $\left(\frac{dn}{dT}\right)$ of the MPTC solution are listed in Table 1.

We have calculated two figures of merit, "FOM" $W = n_2 I/\alpha_0\lambda$ and $T = \beta\lambda/n_2$ to clarify the suitability of the MPTC for photonic devices. According to the literature [9] the values of W (one photon) and T (two-photon) have the characteristic as: $W >> 1$ and $T << 1$. Our results of $W$=2.06 and $T$=0.244, confirming that the MPTC is a good candidate for the optical applications.

It well known that the form of the molecular structure

affects the NLO response of the MPTC [38]. It has been shown that the organometallic complexes show large optical nonlinearities due to their expanded π-electron system and the presence of the d orbital in the central presented transition metal [39-41]. As we expected, our MPTC shows large third–order nonlinear optical properties due to the delocalized electronic states formed by π→π* and d→d* transitions [19-20]. Our sample could be described as good candidate for future application for photonic devices.

Our reported results for $n_2$ and β of the new MPTC are given in Table 2 which can be compared with others new values in literature for different molecules with CW laser excitation [14-15, 35, 38].

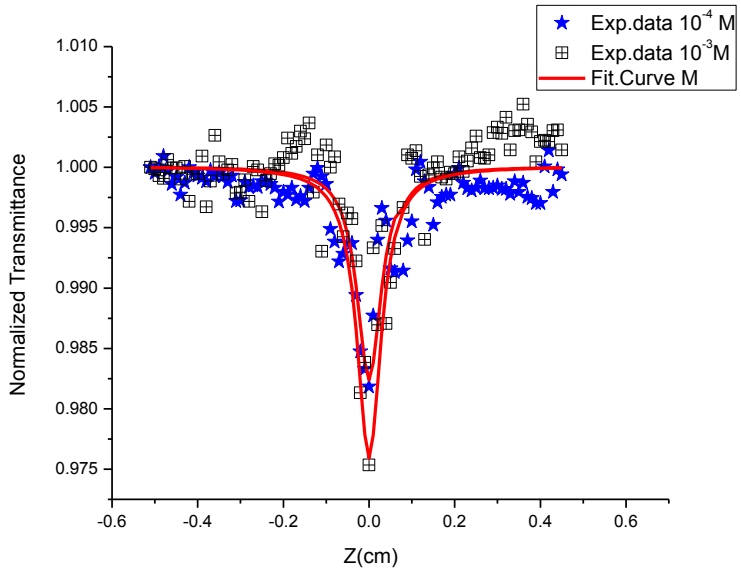


*Fig. 4. Open aperture z-scan data of MPTC in chloroform at two concentrations of concentrations of $10^{-3}$M and $10^{-4}$M (color online)*

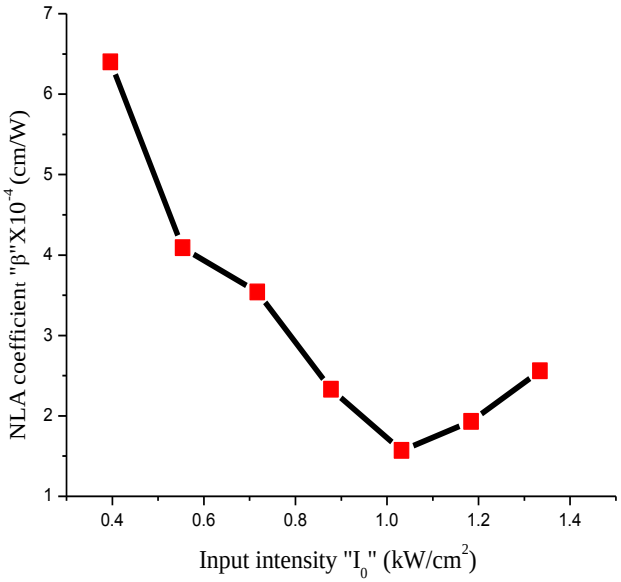


*Fig. 5. The nonlinear absorption coefficient "β" versus on-axis input intensity $I_0$ of MPTC in chloroform (color online)*

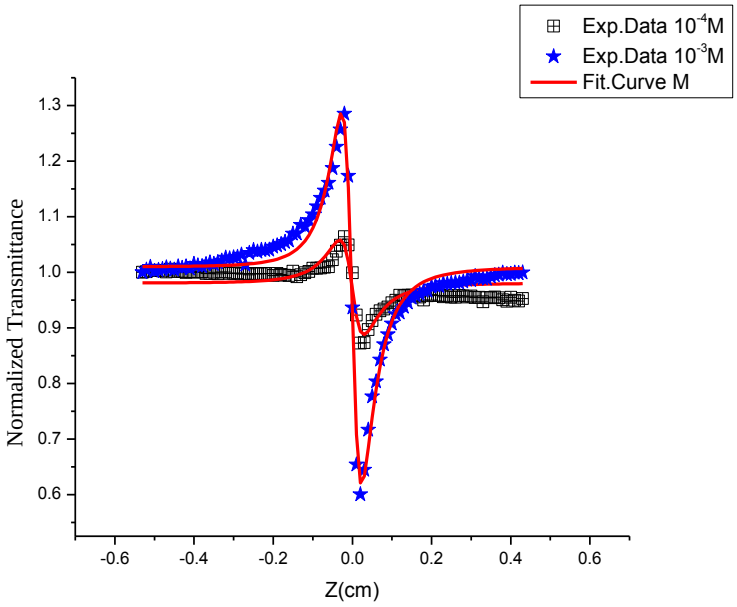


*Fig. 6. Pure (C/O) z-scan data of MPTC in chloroform at two concentrations of concentrations of $10^{-3}M$ and $10^{-4}M$ (color online)*

The observed signals either in the opened or the closed configuration of the pure solvent are neglected comparing to the observed signals of MPTC solation.

*Table 1. The linear absorption coefficient, linear refractive index, $\sigma_g$, $\sigma_{ex}$ and thermal-optic coefficient $(\frac{dn}{dT})$ parameters of MPTC in Chloroform with concentrations of $10^{-3}M$ and $10^{-4}M$*

| Sample concentrations | $\alpha_0$ ($cm^{-1}$) | $n_0$ | $(\frac{dn}{dT})\times10^{-5}$ $(1/k)$ | $\sigma_g$ ($cm^2$) | $\sigma_{ex}$ ($cm^2$) |
|---|---|---|---|---|---|
| $10^{-3}\ M$ | **0.679** | **1.4376** | **5.44** | **$1.13\times10^{-18}$** | **$2.33\times10^{-14}$** |
| $10^{-4}\ M$ | **0.555** | **1.4391** | **1.67** | **$9.22\times10^{-18}$** | **$2.09\times10^{-14}$** |

*Table 2. The calculated nonlinear MPTC in chloroform with concentrations of concentrations of $10^{-3}$ M and $10^{-4}$ M*

| Sample concentrations | $n_2$ ($cm^2/W$) | β (cm/W) | Re ($\chi^{(3)}$) (esu) | Im($\chi^{(3)}$) (esu) |
|---|---|---|---|---|
| $10^{-3}\ M$ | $6.66\times10^{-8}$ | $2.56\times10^{-4}$ | $3.49\times10^{-6}$ | $6.78\times10^{-6}$ |
| $10^{-4}\ M$ | $1.68\times10^{-8}$ | $1.88\times10^{-4}$ | $8.82\times10^{-7}$ | $4.99\times10^{-6}$ |

Regarding, the uncertainties of the $n_2$ and β in Table 2, arise from the measuring of the focal spot size (±5%), linear refractive index (±0.3%), linear absorption coefficient (±5%) and Rayleigh length (±4%). The maximum error in such measurements shouldbe less than 5% for each parameter.

## 4. Conclusions

We have synthesized and characterized a new organo-metallic complex, MPTC. The z-scan method using a CW diode Laser (λ= 635 nm ) was used to calculate the values of $\alpha_0$, $n_0$, $n_2$, β, Re $\chi^3$, Im$\chi^3$ and the thermo-optic coefficient. The studied complex exhibits large NLO response due to the association of the phenanthroline π-electron system, carbonyl (CO) and partially filled d electron set of molybdenum centre ($Mo^{2+}$), which enhances the conjugation of delocalized electrons over the entire framework of complex. The new compound also shows self-defocusing property with negative value of $n_2$.

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