Optical nonlinearities of tetracarbonyl-chromium triphenyl phosphine complex

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(Received 28 November 2016; revised manuscript received 22 January 2017; published online 10 March 2017)

The new tetracarbonyl — chromium-triphenyl phosphine complex was synthesized and characterized using ultraviolet (UV)–visible, Fourier transform infrared (FTIR), and nuclear magnetic resonance (NMR) techniques. The characterization results confirm the molecular structure of the new complex. The *z*-scan measurements were done by diode laser [continuous wave (CW)] to estimate the nonlinear optical parameter (χ^3). The results led to calculate three parameters: the ground-state cross sections (σ_g), the excited-state cross sections (σ_{ex}), and thermo–optic coefficient of the new complex. This study indicated that our complex is a suitable for photonic applications.

Keywords: tetra carbonyl–chromium triphenyl phosphine, Z-scan technique, nonlinear optical materials

PACS: 42.65.–K, 42.70.Nq, 31.15.ap, 42.70.jk **DOI:** 10.1088/1674-1056/26/4/044205

1. Introduction

Organometallic compounds have been attracted several research groups due to their large 3rd susceptibility. The results have encouraged the researchers to use the organometallic in optical devices, such as human eyes and optical sensors protection from high power laser pulses.[1–4] In organometallic compounds, the d electrons of the transition metal would interact with the organic ligand (π–electron). In such metal–ligand system, electrons are free to move and the nonlinear optical (NLO) phenomena come from the interaction between high intensity light and electrons within the molecular units, getting large nonlinear optical effects.[5] The z-scan technique[6,7] was employed to resolve the contribution of both refractive and absorptive parts of the nonlinearity of different materials, such as: the chalcones,[8] hydroxyquinolinium derivatives,[9] fullerenes,[10,11] carbon nanotubes,[12] polyaniline,[13] benzodifuran,[14] alkynyl–ruthenium complexes,[15] TiO_2/polymorphs,[16] and TiO_2/silica glass.[17]

The present paper reports on the synthesis, characterizations and 3rd nonlinear optical study of the tetra carbonyl chromium-triphenylphosphine $Cr(CO)_4(PPh_3)_2$ in dichloromethane. It should be mentioned that the new complex $Cr(CO)_4(PPh_3)_2$ has not been investigated before.

2. Experimental techniques

2.1. Materials

The used chemicals imported from MERCK. The $Cr(CO)_4(PPh_3)_2$ was prepared in the following methods: 0.65-g triphenylphosphine PPh_3, 0.1-g $NaBH_4$, and 0.25-g $Cr(CO)_6$ were placed in 0.25-L flame dried flask, then about 0.015 L of pure ethanol oxygen free was poured over the flask. The mixture in the vessel was connected to evacuating system with nitrogen gas (purity 99.999%) bubbler. The flask was evacuated until ethanol boiling, and then the N_2 gas was inserted into the flask, this operation was repeated five times to remove any remaining oxygen. Then, the mixture was warm up under refluxed at silicon heating oil bath temperature (85 °C) under nitrogen for 3 h, using continuous magnetic stirring, while flushing the flask by a nitrogen flow gas. The final product was filtered hot. The final product (as a solid) was washed 3 times with 0.005 L of distilled cold water and then 3 times with 0.003 L of cold pure ethanol. The final obtained compound looks yellow powder, kept to dray in darkness at room temperature for 24 h.

The obtained material (as shown in Fig. 11) was analyzed by different techniques, such as: Fourier transform infrared (FTIR), nuclear magnetic resonance ^{31}P NMR, and ultraviolet-visible (UV-Vis). The FTIR spectrum was recorded as KBr disc in 400 cm^{-1}–4000 cm^{-1} using Thermo FTIR 6700 instrument with a resolution at 4 cm^{-1} and 64 scan. ^{31}P NMR spectra were acquired by a Bruker Bio spin 400 spectrometer using $CHCl_3$ as solvent. The UV-vis absorption spectrum was recorded in the wavelength range 190 nm–1100 nm using UV-1601 PC Shimadzo Spectrophotometer. The NMR chemical shift for the raw triphenyl phosphine materials shows that, the $^{31}P\{^1H\}$ (200 MHz) δ ppm (s,1P) center at −5.3 ppm, while the NMR chemical shift for the $Cr(CO)_4(PPh_3)_2$ shows that, the $^{31}P\{^1H\}$ (200 MHz) δ ppm

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(s,1P) centers at 74.04 ppm. The melting point of the complex is 295 °C.

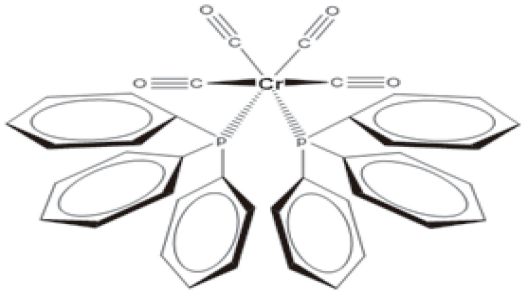


Fig. 1. (color online) Chromium-triphenyl phosphine *cis*-complex structure.

IR (KBr, ν, cm^{-1}): 1877, 1909, and 1918 (C=O), 1089 (P–Ar), 970, 1280, 1433 (P–C), above 3000 cm^{-1} (C–H sym., and asym. stretch); The UV-vis spectrum of $Cr(CO)_4(PPh_3)_2$ shows two maximum absorption peaks around 262 nm and 335 nm.

2.2. *Z*-scan measurements

TEM_{00} Gaussian beam from continuous-wave (CW) diode laser at 26 mW ($\lambda = 635$ nm) was used as the light source. A 10-cm converging lens was used to focus the laser beam. The radius of the beam ω_0 and diffraction length was calculated to be 33.5 μm and 5.5 mm, respectively. The radius of the aperture (r_a) was 0.4 mm and the beam waist (ω_a) on the aperture was 1 mm. The sample cell is 2 mm which was fixed on a computer-controlled translation stage, and it was precisely moved through the focal region of the beam over a length of 6 cm. At the same time, the reference beam energy, and transmitted beam energy were measured using an energy meter (PM300E). Consequently, the transmitted signals were acquired, stored, and later on processed by a computer. The prepared solution was made by accurately weighed amount of the tetracarbonyl-chromium-triphenyl phosphine compounds and dissolved in dichloromethane to obtain samples with a concentration of 10^{-3} M. The experimental set-up was described in full details in Ref. [18].

3. Results and discussion

3.1. NMR, FTIR, and UV-Vis characterizations

The $Cr(CO)_4(PPh_3)_2$ compound was isolated as yellow powder and characterized using the flowing techniques: $^{31}P\{^1H\}$ NMR, FTIR, and UV-Vis spectroscopy. The $^{31}P\{^1H\}$NMR spectrum of the triphenyl phosphine raw materials gave one singlet peak for P centered at −5.21 ppm, whereas the $^{31}P\{^1H\}$NMR spectrum of the $Cr(CO)_4(PPh_3)_2$ gives also one singlet for P centered at 74.04 ppm, this shift in ^{31}P peak gives a strong evidence for the complex formation. Figure 2(a) shows the FTIR spectrum of the raw materials. The small window is the infrared spectrum of the chromium hexacarbonyl, [Cr $(CO)_6$]. The main features regarding the carbonyl broaden vibration group frequency is observed and centered at 1960 cm^{-1}. Concerning the second spectrum in the large window which presents the triphenylphosphine (PPh_3) raw material, the band observed at 1877 cm^{-1} is very week in comparison with complex infrared spectrum which will be shown later. The remaining vibration bands are due to the aromatic rings in the PPh_3 and these bands are consistent with reported literature. Figure 2(b) shows the FTIR spectrum of the $Cr(CO)_4(PPh_3)_2$ with the mean characteristic bands at 1877, 1909, and 1918 cm^{-1}. These three bands are assigned to the three different carbonyl bands in the *cis*-$Cr(CO)_4(PPh_3)_2$ complex, these bands consider to be a good indication of completion of complexion reaction, the band at 1089 cm^{-1} is assigned to aromatic rings in the complex (P–Ar), the other two bands at 970 cm^{-1}, 1280 cm^{-1}, and 1433 cm^{-1} were assigned to rocking bend, symmetric stretching, and asymmetric deformation of P–C groups, respectively. The Cr–P stretching frequency has been observed at about 435 cm^{-1} which is definitely confirming the complexion reaction which is not seen in the raw materials. Finally, the C–H group shows symmetric and asymmetric absorptions above 3000 cm^{-1}.

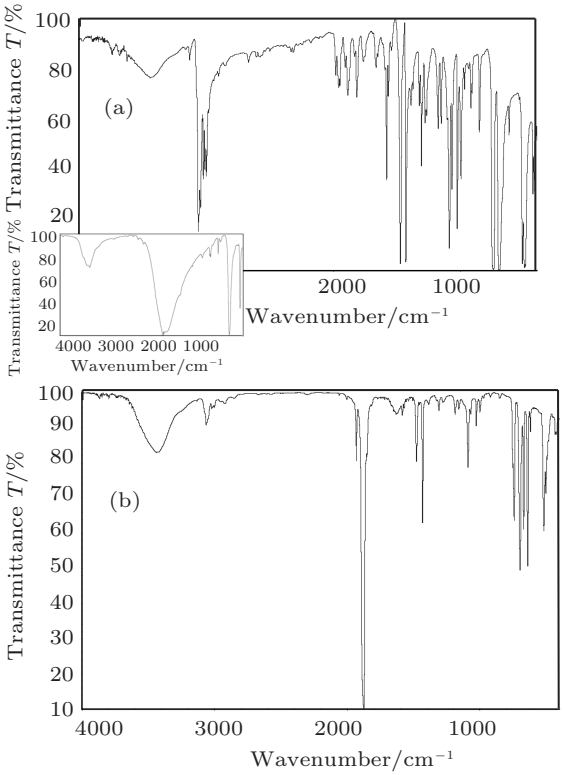


Fig. 2. The FTIR spectra of (a) the raw materials and (b) *cis*-tetracarbonylchromium-triphenyl and taken as KBr Disk.

The UV-Vis spectrum of $Cr(CO)_4(PPh_3)_2$ (Fig. 3) shows two maximum absorption peaks at around 235 nm and 262 nm. These transitions are assigned to $\pi \rightarrow {}^*\pi$ and $n \rightarrow {}^*$d transitions in the complex, respectively.[19–21]

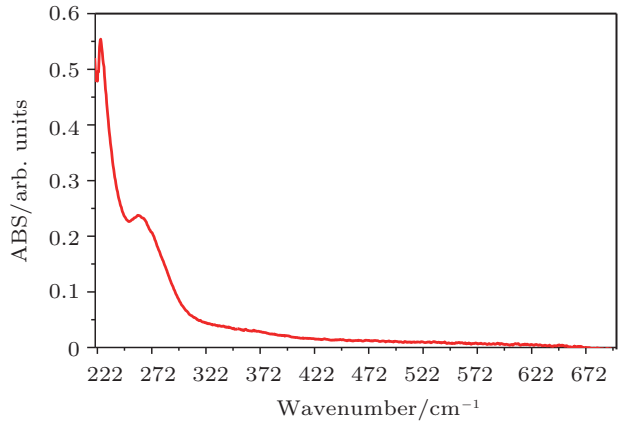


Fig. 3. (color online) The ultraviolet-visible spectrum of the *cis*-tetracarbonylchromium-triphenylphosphine in dichloromethane.

3.2. Nonlinear measurements

In the open aperture (OA) z-scan experiment, the $Cr(CO)_4(PPh_3)_2$ complex dissolved in dichloromethane at concentration of 10^{-3} M, with input intensity of $I_0 = 936$ W/cm^2. The transmitted intensity measured by the detector is sensitive only to the intensity variation. Here, the transmission is symmetric at the focus point ($z = 0$), where it becomes at the minimum value, the data show the dependent of the transmission with z (Fig. 4).

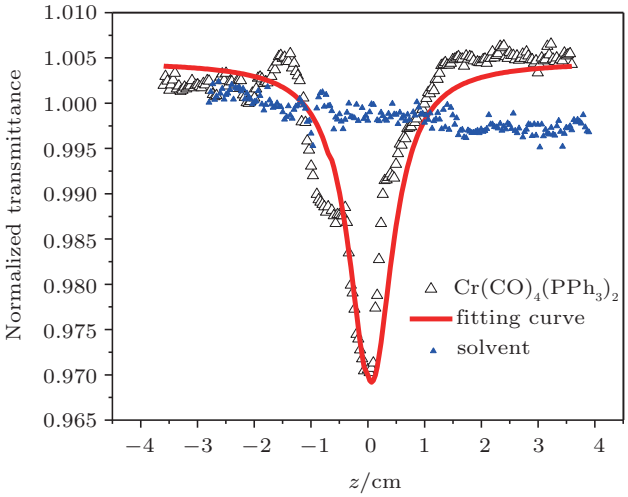


Fig. 4. (color online) The open aperture z-scan data of the tetracarbonylchromium-triphenyl phosphine complex in dichloromethane.

Theoretical fit was performed to the experimental data (Fig. 4), to estimate the nonlinear optical absorption coefficient "β" using the following equation[6,7]

$$T(z) = \sum_{m=0}^{\infty} \frac{(-q_0)^m}{(m+1)^{3/2}}. \tag{1}$$

For $q_0 < 1$, Where $q_0(z)$ is a parameter function of I_0, L_{eff}, and β:

$$q_0(z) = \frac{I_0 L_{\text{eff}} \beta}{(1 + z^2/z_0^2)}. \tag{2}$$

Solving the summation and for $\alpha_0 \ll 1$

$$T(z) = 1 - \frac{(I_0 L_{\text{eff}} \beta)}{\left[2^{3/2}\left(1 + z^2/z_0^2\right)\right]}. \tag{3}$$

In Eqs. (1)–(3), $L_{\text{eff}} = (1 - \exp(-\alpha_0 L))/\alpha_0$ is the effective thickness of the sample, L is the thickness of the sample, α_0 is the linear absorption, $z_0 = \pi\omega_0^2/\lambda$ is the diffraction length of the beam and $I_0 = 936$ W/cm^2 is the power density at focus $z = 0$. In Fig. 4, the "symbols" indicate experimental data, while the "solid line" indicates the fitting curve obtained by Eq. (3).

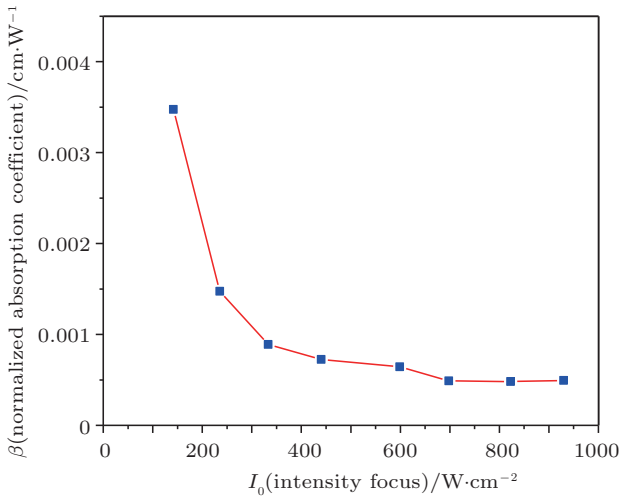


Fig. 5. (color online) Nonlinear coefficient β versus on-axis input intensity I_0 of the tetracarbonyl chromium-triphenyl phosphine complex in dichloromethane.

Figure 5 shows the dependence of excitation intensity (I_0) on nonlinear absorption coefficients (β). The values of β decrease drastically with increasing I_0. This is a result of sequential two-photon absorption (TPA). In the present case, the nonlinearity is due to the TPA and excited state absorption (ESA) assisted reverse saturable absorption (RSA) process.[22] According to the literature, the RSA process may explain on the bases of famous five-level model in the organic compounds with extended π–electron system.[22–24] The basic condition of the RSA process is $(\sigma_{\text{ex}}) > (\sigma_{\text{g}})$. It is well known that the β coefficient is related to $\Delta\sigma$ by the following Eq. (4),[25–27]

$$\beta = \frac{\lambda N_0 \Delta\sigma}{4\pi I_{\text{s}}}, \tag{4}$$

where $\Delta\sigma = \sigma_{\text{ex}} - \sigma_{\text{g}}$, N_0 is the total concentration of the samples in a cubic unit (cm^3), and $I_{\text{s}} = hc/\lambda\sigma_{\text{g}}\tau$, where hc/λ is the pump–photon energy, τ is the excited lifetime and taken to be 1 ms (triplet state decay time). The $\sigma_{\text{g}} = \alpha_0/N_0$ and found to be $\sigma_{\text{g}} = 5.65 \times 10^{-19}$ cm^2 for the Cr(CO)4(PPh3)2 complex. Using Eq. (4), the σ_{ex} was calculated at 635 nm and found to be $\sigma_{\text{ex}} = 8.82 \times 10^{-14}$ cm^2. This confirms that the $\sigma_{\text{ex}} \gg \sigma_{\text{g}}$ (five orders), which is in good agreement with the conditions for observing RSA.

To evaluate the sign and magnitude of the nonlinear refractive index n_2 of our complex, the normalized transmittance T of closed aperture (CA) is given by[6,7,28]

$$T(z, \Delta\phi) = 1 + \Delta\phi_0 \frac{4X}{(X^2+9)(X^2+1)}, \tag{5}$$

where $X = (Z/Z_0)$ and $\Delta\phi_0$ is on-axis nonlinear phase shift. The normalized CA data are fitted with Eq. (5) to obtain $\Delta\phi_0$ values. The n_2 coefficient is related to $\Delta\phi_0$ by Eq. (6)

$$n_2 = \frac{\lambda\Delta\phi_0}{2\pi I_0 L_{\text{eff}}}. \tag{6}$$

In Fig. 6 the solid line and the symbols indicate the fitting curve and the experimental data, respectively.

The deduced values of the β and the n_2 were used to calculate the corresponding real and imaginary parts of the χ^3 with the relations given in the literature[6,7]

$$\text{Re}\,\chi^3\ (\text{esu}) = (10^{-4}\ \varepsilon_0 c^2 n_0^2/\pi) n_2\ (\text{cm}^2/\text{W}), \tag{7}$$

$$\text{Im}\,\chi^3\ (\text{esu}) = (10^{-2}\ \varepsilon_0 c^2 n_0^2 \lambda/4\pi^2)\beta\ (\text{cm/W}), \tag{8}$$

where ε_0 is the vacuum permittivity and c is the speed of light in vacuum.

The values of α_0 were determined according to the similar method described in Ref. [18]. The linear index n_0 was obtained by using commercial Abbe refract meter. The new values of α_0, n_0, n_2, β, $|\text{Re}\,\chi^3|$ and $|\text{Im}\,\chi^3|$ are listed in the following Table 1.

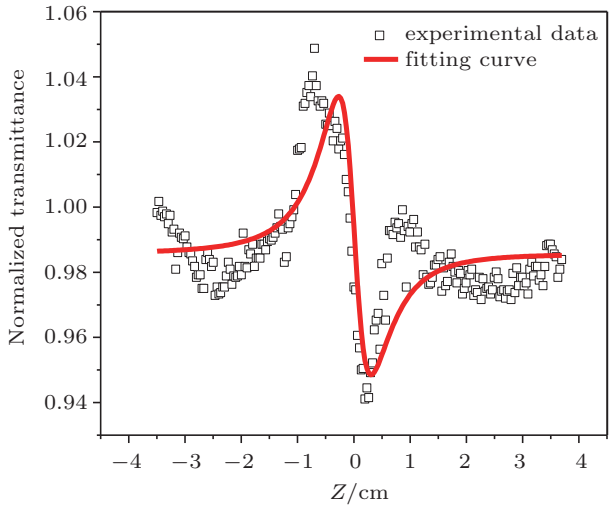


Fig. 6. (color online) Closed aperture data of the tetracarbonyl chromium-triphenyl phosphine complex in dichloromethane.

Table 1. The nonlinear coefficients of tetracarbonyl chromium-triphenyl phosphine complex ($Cr(CO)_4(PPh_3)_2$) in dichloromethane at concentration of 10^{-3} M.

Sample	α_0/cm^{-1}	n_0	$n_2/(\text{cm}^2/\text{W})$	$\beta/(\text{cm/W})$	$\text{Re}\,\chi^3/\text{esu}$	$\text{Im}\,\chi^3/\text{esu}$
$Cr(CO)_4(PPh_3)_2$	0. 34	1.4234	-1.06×10^{-8}	4.85×10^{-4}	5.44×10^{-7}	1.26×10^{-5}

It is clearly evident from Fig. 6 that the tetracarbonyl chromium-triphenyl phosphine exhibits peak–valley characteristics. This configuration is a direct indication of negative n_2 and ca be considered as a self-defocusing material around 635 nm. The defocusing effect rose from the absorption of the laser beam (CW) propagating through an absorbing medium. This led to variation in the n_2 where the sample works as thermal lens resulting in severe phase distortion of the propagating beam.[27,28]

In this work, as the CW laser is used, the nonlinearity in our sample is considered as a thermal origin. The thermal nonlinearity n_2 is related to the thermo–optic $(\text{d}n/\text{d}T)$ by the following equation[29]

$$\left(\frac{\text{d}n}{\text{d}T}\right) = \frac{4n_2\kappa}{\alpha_0\omega_0^2}, \tag{9}$$

where κ is the thermal conductivity of the solvent ($\kappa = 0.139$ W/mK). Using Eq. (9), the value of the $(\text{d}n/\text{d}T)$ of the tetracarbonylchromium-triphenyl phosphine complex has been calculated to be $1.54\times10^{-5}(1/\kappa)$.

In addition to the thermal effect, the NLO response of the tetracarbonylchromium-triphenyl phosphine complex is raised from a lot of structure factors,[30] and the non-localized π–electron with the heavy central metal.[31–33] The experiment was repeated to trace any contribution for the used solvent, but no signals were observed as seen in Fig. 4.

In the present paper, the nonlinear optical coefficients of our new complex — tetracarbonylchromium-triphenyl phosphine in dichloromethane compound listed in Table 1 were compared with previous results for molecules with the CW laser excitation.[33–36]

4. Conclusions

In conclusion, the nonlinear measurements of novel tetracarbonyl chromium triphenyl-phosphine are conducted by diode laser ($\lambda = 635$ nm). Depending on the experimental results, the values of α_0, n_0, n_2, β, $\text{Re}\,\chi^3$, $\text{Im}\,\chi^3$, and the thermo–optic coefficient are calculated by fitting the experimental data. We found that the tetracarbonyl chromium triphenyl-phosphine exhibited large third-order susceptibility, due to the phenyl groups. Our new sample exhibits self-defocusing property with negative value of the n_2 at $\lambda = 635$ nm with potential applications in optoelectronic devices.

Acknowledgements

We thank Prof. I Othman for his permanent encouragement, also to Prof. M K Sabra for his useful discussions.

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