

## Second Harmonic Hyper - Rayleigh Light Scattering (HRS) in organic materials

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### ABSTRACT

In this paper, an optical setup to produce harmonic hyper-Rayleigh light scattering (HRS) from organic molecules in solution has been built up. In principle, HRS measures contribution coefficients of dipole and octupole parts. The nonlinear susceptibility of the second order of six organic molecules in solution from different chemical components such as Pyridinium, Quinolinium groups and organic Borone complexes has been determined. The nonlinear susceptibility measurements help to discover and select the most efficient molecules which can be used later as polymer matrices.

**Key words:** Rayleigh scattering, harmonic light, organic materials, nonlinear susceptibility.

## تشنتت رايلى التوافقي الشديد الثاني في المواد العضوية

فادي قمر

قسم الفيزياء - كلية العلوم - جامعة دمشق - سورية

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### الملخص

جرى في هذه البحث إعداد وبناء تجربة ضوئية لدراسة تشنتت رايلى التوافقي الشديد الناتج عن جزيئات عضوية محلولة بمحل مناسب. تتضمن دراسة تشنتت رايلى التوافقي الشديد من حيث المبدأ دراسة إسهامات معاملات ثنائي القطب وثمانية الأقطاب للمركبات العضوية. وقد دُرست الطواعية اللاخطية لستة مركبات كيميائية عضوية مختلفة من زمرة اليردينوم والكوانتيلينيوم ومعقدات البور العضوية. تساعد دراسة الطواعية اللاخطية على اكتشاف الجزيئات الأكثر كفاءة وتحديدتها لتوليد التوافق الثاني لضوء الليزر الذي يمكن استخدامه لاحقاً في تصنيع المعقدات الكيميائية (البوليمرات).

الكلمات المفتاحية: تشنتت رايلى، توافقات الضوء، المركبات العضوية، الطواعية اللاخطية.

## 1. Introduction

The need for efficient systems that can manipulate and modulate an incoming optical signal for a rapid optical telecommunications and information technologies [1], is driving the research toward finding materials that interact strongly with the electric field of an incident laser radiation and generate nonlinear optical material (NLO) responses. NLO phenomena include a large number of effects, e.g., second and third harmonic generation and electro-optic (EO) change of refractive index (i.e. low dielectric constant resulting in a fast response time of (EO) devices [2,3]. The development of organic-based electro-optic materials with high performance, requires both (i) an optimization of the NLO properties of the molecular chromophore of which the material is made and/or (ii) an optimization of the setup. Efficient molecular systems and materials have been developed in recent years, providing high second-order NLO effects at both the molecular [4] and macroscopic levels [5]. The first generation of organic chromophores for second-order NLO have a general structure in which a  $\pi$ -conjugated bridge links together both a strong electron-accepting (A) unit and a strong electron-donating (D) one, producing A- $\pi$ -D systems. Later, other structures have been proposed, including octupolar [6]  $\Lambda$ -shape[7] and tetrathia helicenes molecules[8]. The first hyperpolarizability  $\beta$  which describe the second order NLO response at the molecular level can be measured by different techniques. One of the most popular techniques at the present is HRS or second harmonic light scattering [9-18]. However, a single wavelength in the near infrared (such as 1064 nm the output wavelength of Nd:YAG laser system) are usually used to perform HRS measurements [19]. This result in  $\beta$  values that are strongly influenced by (two photon) resonant enhancement as for typical NLO chromophores having an intra-molecular charge-transfer (CT) transition in the visible region. This complicates the comparison of  $\beta$  between different molecules and the assessment of their potential for EO applications [19]. To avoid the resonance effect on  $\beta$ , HRS measurements have been carried out at a wavelength further in the infrared (IR) were first performed at 1500 nm [20], and later at 1907 nm (the fundamental wavelength accessible by Raman shifting the Nd:YAG output in H<sub>2</sub> cell) [21]. However, the wavelength-dependence of the first hyperpolarizability  $\beta$  is still not well-understood [18], therefore, there is a strong need for detailed and accurate measurements of  $\beta$  dispersion of organic molecules over a wide wavelength range around and beyond their absorption resonance.

In this paper, new optical setup to produce hyper-Rayleigh light scattering at near 1 $\mu$ m using 1907 nm (the output of H<sub>2</sub> cell pumped by Nd:YAG pulsed laser) as source has been developed and optimized. Second harmonic susceptibility  $\beta$  for two organic materials from different chemical groups has been determined for the first time using the previous setup.

## 2. Theoretical background

The chromophores are molecules with intra-molecular charge transfer, molecular clusters composed of donor and acceptor of electrons connected by a chain of conjugated  $\pi$  electrons. These molecules can be purely organic or organo-metallic. It is known that the nonlinear properties of macroscopic material depend on the molecular level of polarization of each chromophore. In the case of the second order NLO, this ability is related to quadratic hyperpolarizability tensor. The chromophore molecules are strongly asymmetric and with a permanent dipole moment. Thus, when applying an electric field on these molecules, the charge transfer, and therefore the induced dipole moment depend on the orientation of the field. In the case of an electric field oscillating at angular frequency  $\omega$ , one can observe an oscillation of the dipole moment induced asymmetric function of time (i.e. nonlinear response). This nonlinear response is the source of the molecular quadratic hyperpolarizability of the second order. Generally, the multi-linear expression of the dipole moment  $P$  in term of optical electric field is given by [6]:

$$P = P_i + \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l + \dots \quad [1]$$

The second-order nonlinearity is characterized at the molecular level by susceptibility term  $\beta$  called the hyperpolarizability. The values of  $\beta$  can stretch thousands of electrostatic units. If the molecule is not polarized (ie the electron cloud is spread out evenly), then it is centro-symmetric and therefore has zero value of  $\beta$  (eg carbon dioxide CO<sub>2</sub>). Otherwise,  $\beta$  contains two contributions, dipole and octupole [6] as shown in figure (1) and its value is:

$$\langle b^2 \rangle = \underbrace{\frac{2}{9} b^2}_{\text{dipolar}} \quad \underbrace{+ \frac{2}{21} b^2}_{\text{Octupole}} \quad [2]$$

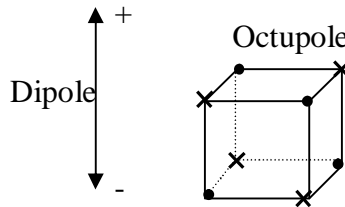


Figure (1) Dipole and Octupole parts

In the case of second harmonic generation (SHG) of optical wave at frequency  $\omega$ ,  $I_{2\omega}$  is proportional to  $[N \langle \beta^2 \rangle (I_\omega)^2]$ , where  $N$  molar concentration per unit of volume (mmol/L), and  $\langle \beta^2 \rangle$  is the mean square of the quadratic hyperpolarizability. In practice, to determine  $\beta$  the slope of  $I_{2\omega} = f (I_\omega)^2$  gives  $m = N \cdot \beta^2$ . The average slope for the sample  $P_s$  and for well known solution (Ethyl Violet)  $m_{\text{etv}}$  can be measured and then the hyperpolarizability for the sample  $\beta_s$  can be calculated from [22]:

$$\frac{m_s}{m_{\text{etv}}} = \frac{N_s \beta_s^2}{N_{\text{etv}} \beta_{\text{etv}}^2} \quad \text{or} \quad \frac{\beta_s}{\beta_{\text{etv}}} = \sqrt{\frac{N_{\text{etv}} m_s}{N_s m_{\text{etv}}}} \quad [3]$$

### 3. Experimental setup

Nd: YAG multimode pulsed laser was used as the pump source at the wavelength of 1064 nm, with a repetition rate of 10Hz and pulsed width of 5ns with 400mJ energy per pulse. The laser beam is aligned and directed to the center of Raman cell using two staring mirrors  $M_1$  and  $M_2$  and 1m focal length converging lens  $L_1$  located in between to focus the beam into nearly the middle of the Raman cell that have pressure of 40 bar (figure 2). The output radiation from the cell consists of wavelengths of 1.9  $\mu\text{m}$ , visible light (blue and green), UV and some remaining pump wavelength at 1.06  $\mu\text{m}$ . Special filter RG1000 and collimating lens system  $L_2$  are used to filter and collimate the backscattered Raman emission at 1.9  $\mu\text{m}$ . The energy of 1.9  $\mu\text{m}$  collimated emitting beam was 10mJ. Another, two staring dielectric mirrors  $M_3$  and  $M_4$  were used to direct the beam into a horizontal polarizer to ensure that the laser radiation is horizontally polarized at previous wavelength (i.e. 1.9  $\mu\text{m}$ ). The beam then passes through a half-wave plate rotated by a stepper micro-controlled motor and then through an  $A_v$  scanner vertically polarized (Analyzer) as it is shown in figure 3. The polarizer and the analyzer are crossed when the neutral lines of the half-wave plate are parallel to the polarizer  $P_H$ . When the half-wave plate rotates through an angle  $\theta$ , the polarization rotates  $2\theta$  due to the phase shift of the blade. Therefore, to make the measurements, the engine of the blade was turned 45 degrees so that the polarization is rotated  $90^\circ$ . After the analyzer, the beam passes through a glass slide which reflects about 10% of the incident signal. The reflected beam is focused by a converging lens  $L_3$  of focal length of 150 mm, into a black box then passes through to the first near infrared photomultiplier (reference beam).

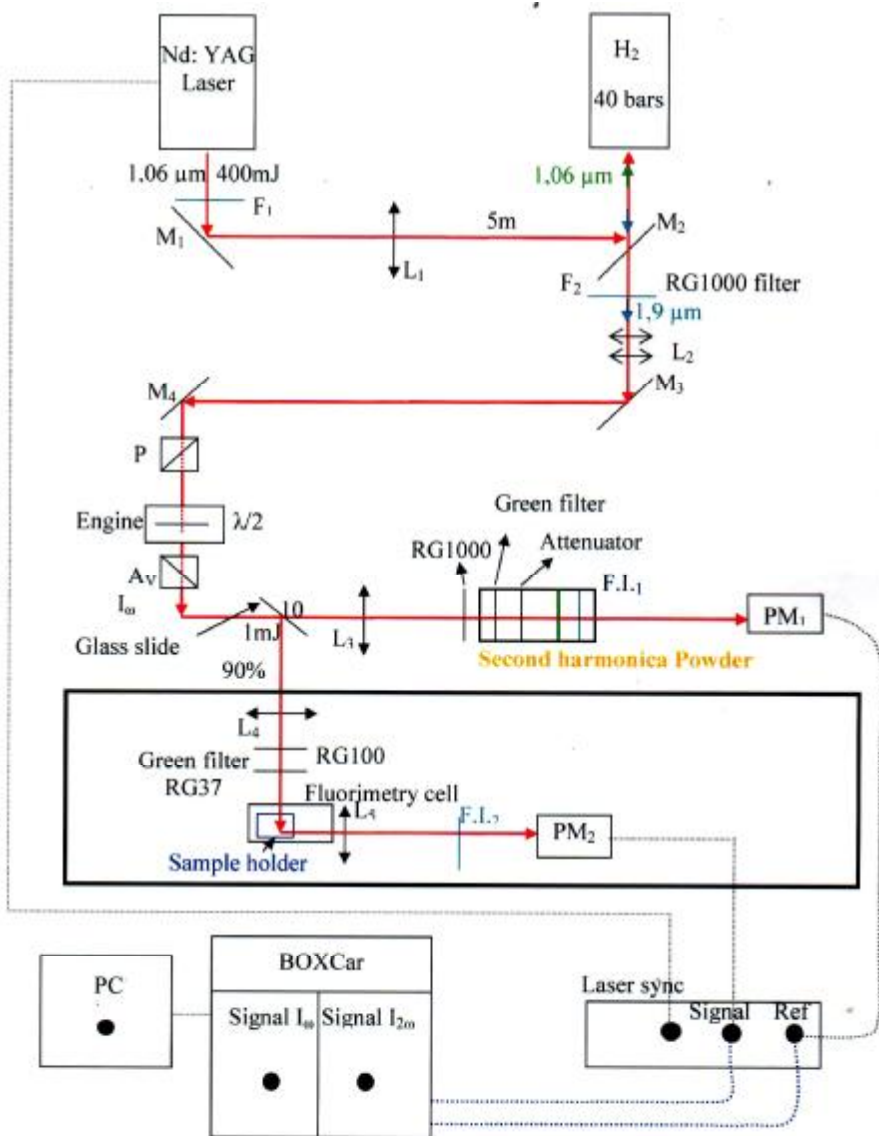
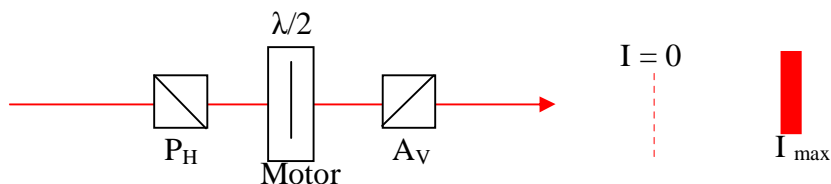
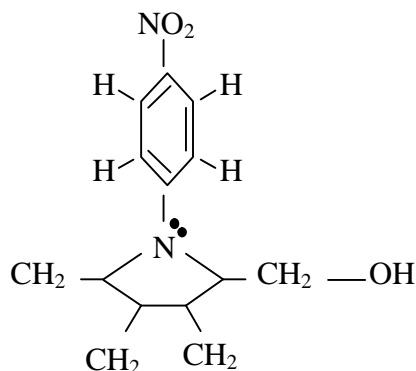


Figure (2) Setup of the experiment.



**Figure (3) controlling the polarization in the setup**

The black box contains a filter RG1000 in order to pass the wavelength of  $1.9\mu\text{m}$ , a green filter (to eliminate green light), attenuator (to decrease the intensity of the beam), a powder MPN (a crystal powder an organic name N-4-nitrophenyl-L-prolinol, shown in figure (4)) to generate a second harmonic for  $1.9\mu\text{m}$  laser and finally an interference filter  $\text{FI}_1$  centered on  $954\text{ nm}$  (to pass only the second harmonic wavelength).



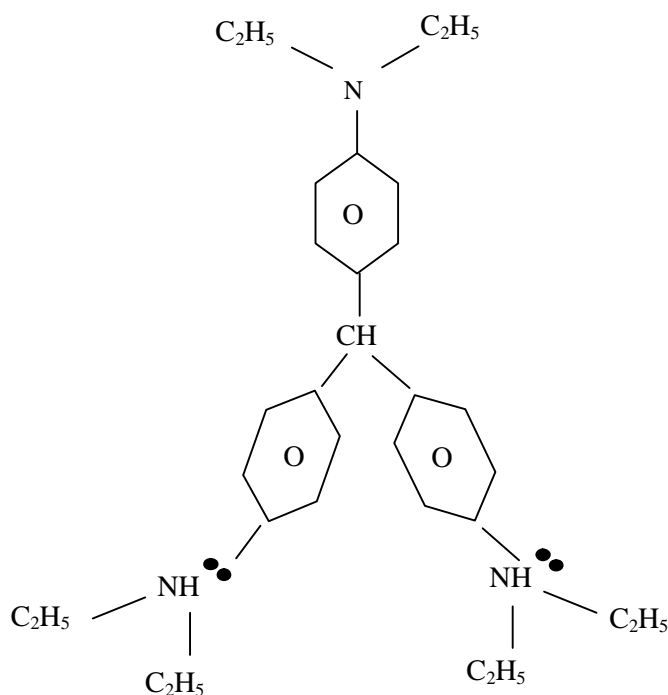
**Figure (4) Chemical structure of the powder second harmonic MPN**

The second beam passes through two filters a RG1000 and BG38 Green for ensuring that only  $1.9\mu\text{m}$  wavelength was passing through the sample (this filter transmits only 40% of the signal at  $1.9\mu\text{m}$ , which is sufficient for the experiment). The beam was then focused by  $L_4$  lens of  $50\text{ mm}$  focal length on a tank vessel (which contains the solution to study). A collecting lens  $L_5$  of  $100\text{ mm}$  focal length collects the maximum harmonic signal after passing through an interference filter centered on  $954\text{ nm}$   $\text{FI}_2$ . The final beam will be detected by a second infrared photomultiplier  $\text{PM}_2$  to get the signal of the second harmonic ( $I_{2\omega}$ ). The final energy on the tank was improved to reach about  $5\text{mJ}$ . The two photo-detectors were connected to box-car synchronized with fundamental laser beam. The signal then sent to

a computer which has a special program to analyze the data and draw  $I_{2\omega}$  for solution as function ( $I_{\omega}^2$ ) of the reference. The slope P can be obtained from the slope of the straight line of the curve.

#### 4. Result and discussions

The standard solution that is used as a reference was ethyl violet dissolved in Chloroform  $\text{CHCl}_3$  (figure (5)). It has a very strong non-linearity which allows to compare the nonlinearity of this molecule with other studied organic molecules. This molecule has the advantage of being cheap and absorbs around 600 nm which is far from scattered wavelength.



**Figure (5) Chemical Structure of Ethyl Violet**

The Ethyl violet that was prepared has the following characteristics:

<b>Colour</b>	<b>Violet</b>
Name of solvent	$\text{CHCl}_3$
Molecular Weight (g/mol)	492.14
$N_{\text{etv}}$ (mmol/L)	8.05
$\beta$ (u.es)	$170 * 10^{-30}$



Different types of organic molecules (supplied by Chemistry Department at Catania University, Italy) were dissolved in Chloroform  $\text{CHCl}_3$ . Names, properties and concentration of these used solutions are shown as follows:

a) (2-(2-[5'-(N,N-dimethylamino) - (2,2'-bithiophen)-5-yl]vinyl) -1-methylpyridin-1-ium iodide), and it is shown in figure (6), and its characteristics are:

Colour	Dark blue
Name of solvent	$\text{CHCl}_3$
Molecular Weight (g/mol)	538.55
$N_s$ (mmol/L)	5.12

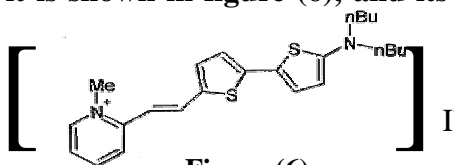


Figure (6)

b) (2- (2- [5'- (N, N- dimethylamino) -(2,2'-bithiophen)-5-yl]vinyl)-1-methylquinolin-1-ium iodide), as it is shown in figure (7):

Colour	Dark green
Name of solvent	$\text{CHCl}_3$
Molecular Weight (g/mol)	588.61
$N_s$ (mmol/L)	5.2

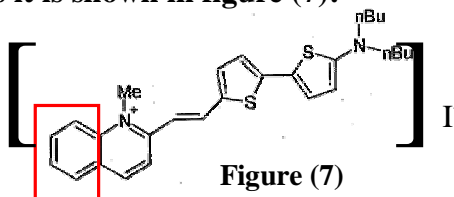


Figure (7)

c) Nepla Carbo-nona Boro-hexadeca Hydro-Cobalt,  $\text{CoC}_7\text{B}_9\text{H}_{16}$ , as it is shown in figure (8):

Colour	Yellow
Name of solvent	$\text{CHCl}_3$
Molecular Weight (g/mol)	256.43
$N_s$ (mmol/L)	5.34

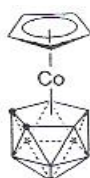


Figure (8)

d) Octo Carbo - nona Boro - octadeca Hydro - Cobalt,  $\text{CoC}_8\text{B}_9\text{H}_{18}$ , as it is shown in figure (9):

Colour	Yellow
Name of solvent	$\text{CHCl}_3$
Molecular Weight (g/mol)	270.46
$N_s$ (mmol/L)	5.15

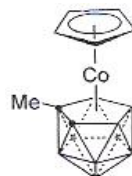


Figure (9)

e) Trideca Carbo - nona Boro - eozan Hydro - Cobalt,  $\text{CoC}_{13}\text{B}_9\text{H}_{20}$ , as it is shown in figure (10):

Colour	Dark Yellow
Name of solvent	$\text{CHCl}_3$
Molecular Weight (g/mol)	332.53
$N_s$ (mmol/L)	5.27

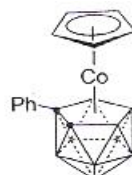
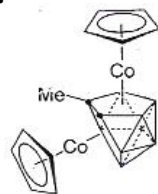


Figure (10)

**f) Trideca Carbo-octa Boro - doecozan Hydro - dicobalt,  $\text{Co}_2\text{C}_{13}\text{B}_8\text{H}_{22}$ , as it is shown in figure (11):**

Colour	Yellow
Name of solvent	$\text{CHCl}_3$
Molecular Weight (g/mol)	382.67
$N_s$ (mmol/L)	5.07



**Figure (11)**

To calculate the hyperpolarizability  $\beta$  of previous chemical components, first the sample solution was placed on the sample holder (see fig.2). Then the half-wave plate engine was turned on to perform a scan from 0 to 45 ° which vary the incident intensity. This is allows to draw the curve of  $I_{2\omega}$  for the sample (the signal from  $\text{PM}_2$ ) in terms of  $(I_{\omega})^2$  that was given by the reference doubling powder (the signal from  $\text{PM}_1$ ). The two detectors,  $\text{PM}_1$  and  $\text{PM}_2$  were connected directly to a computer which contains special software to find the best fit of the previous curve and calculatef slop m. To obtain an accurate measurements the slope for the standard sample solution (ethyl violet), then for sample and again for the standard sample solution were calculated five times (by repeating the experiment) and the average value of the slope was calculated and applied to equation [3]. The following table gives the resultants hyperpolarizability  $\beta$  for the studied samples:

$\beta_{2-(2-[5'-(N,N\text{-dimethylamino})-(2,2'\text{-bithiophen})-5\text{-yl}]\text{vinyl})-1\text{-methypyridin-1-ium iodide}}$	$326 \pm 9 * 10^{-30}$ u.es
$\beta_{2-(2-[5'-(N,N\text{-dimethylamino})-(2,2'\text{-bithiophen})-5\text{-yl}]\text{vinyl})-1\text{-methyquinolin-1-ium iodide}}$	$375 \pm 6 * 10^{-30}$ u.es.
$\beta_{\text{CoC}_7\text{B}_9\text{H}_{16}}$	$92 \pm 5 * 10^{-30}$ u.es.
$\beta_{\text{CoC}_8\text{B}_9\text{H}_{18}}$	$274 \pm 12 * 10^{-30}$ u.es.
$\beta_{\text{CoC}_{13}\text{B}_9\text{H}_{20}}$	$454 \pm 15 * 10^{-30}$ u.es.
$\beta_{\text{Co}_2\text{C}_{13}\text{B}_8\text{H}_{22}}$	$1100 \pm 20 * 10^{-30}$ u.es.

The hyperpolarizability values of the presented samples are not yet calculated theoretically to compare them with the modeling methods of quantum chemistry, but their order of magnitude can be checked by making a comparison between the molecules themselves and by comparing them with similar group which has been published in some reference papers. Unfortunately, the amount of supplied tested samples were too little and not enough to do further study of hyperpolarizability values for the sample in different solvents or as function of solution concentration. However, the results obtained from this new optical setup show that iodides salts presented here (the first two molecules) have good nonlinear properties nearly twice of that for

Ethyl violet and the order of magnitude of the results were in agreement with ref [23, 24]. The slight increase in hyperpolarizability value of (2- (2- [5'-(N, N- dimethylamino) - (2,2'- bithiophen) - 5 - yl] vinyl) -1- methyquinolin-1- ium-iodide) comparing with (2- (2- [5'-(N, N- dimethylamino) - (2,2'- bithiophen) -5- yl] vinyl) -1 - methypyridin-1-ium-iodide) is due to the increasing of the length of the conjugated interconnect enhances of the optical nonlinearity [23]. On the other hand organic boron complexes show that the more the number of carbon, hydrogen atoms conjugated, the higher the electron clouds (longer conjugated interconnect) thus the better value of the hyperpolarizability  $\beta$ . In addition, comparing  $\beta$  of the last two components (i.e  $\text{CoC}_{13}\text{B}_9\text{H}_{20}$  and  $\text{Co}_2\text{C}_{13}\text{B}_8\text{H}_{22}$ ) shows that the polarizability of Cobalt atom is much higher than that for Bohr atom, therefore increasing the number of metallic atoms leads to enhance the polarizability of the whole solution and gives higher value of  $\beta$ . Again, the order of magnitude of organic boron complexes are measured here were in agreement with ref [25].

### 5. Conclusion

New optical set up was arranged to measure second harmonic hyper-Rayleigh scattering of nonlinear organic molecules pumped by 10 nj of 1.9  $\mu\text{m}$  laser. The measurements were used to calculate the hyper-polarizability of the studied molecules. The studied iodides salts and organic Borone complex molecules showed good nonlinear properties compared to the well known nonlinear reference solution (Ethyl violet), and these chromophores could be recommended to be used in manufacturing nonlinear polymers work operating at 2 $\mu\text{m}$  wavelength of light. Results also confirm that the denser electron clouds in organic molecule, the higher hyperpolarizability that is why  $\text{Co}_2\text{C}_{13}\text{B}_8\text{H}_{22}$  has the best  $\beta$  of about  $1100 * 10^{-30}$  u.es which makes it an excellent candidate for different nonlinear applications.

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