

Optical Setup for Investigating the Hyperpolarizability of Organic Nanostructure Materials in Solutions Using Electric Field Induced Second Harmonic Generation

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Abstract: In this paper, an optical setup for electric field-induced second-harmonic generation (EFISH) at 1.9 μm experiment was arranged and used to investigate and determine the hyperpolarizability of some nanostructure organic components in two different solutions. First, a laser beam at 1.9 μm was generated by pumping a hydrogen Raman cell pressurized to 55 bar with 10 Hz Q-switched Nd: YAG nanosecond laser operating at $\lambda = 1.064 \mu\text{m}$. Next, the generated laser beam was aligned with all optical components within the assembly. The final step was to optimize the beam's power and polarization at the center of the EFSH cell. Different nanostructure organic samples in solutions were prepared with nearly the same standard concentration of about 5 mmol/L to be investigated under the optimized system. Two solvents were used in this work, dichloromethane, or DCM (CH_2Cl_2), and chloroform, or trichloromethane (CHCl_3). First, the harmonic order hyperpolarizability of five organic molecules in solutions with different chemical components such as quinolinium groups and organic boron complexes (supplied by the Chemistry Department at Catania University, Italy) were experimentally investigated experimentally. Only component (2-(2-[5'-(N,N-dimethylamino)-(2,2'-bithiophen)-5-yl]vinyl)-1-methylquinolin-1-ium iodide) in chloroform showed a significant difference in Maker fringes amplitude of the applied electrical field in comparison with fringes of its pure solvent. The value of $\mu\beta$ for this component has been calculated as 1320×10^{-48} esu. This value indicates that the component is a suitable candidate for use in second-harmonic generation imaging for biological applications.

Keywords: Electric field-induced second-harmonic generation (EFISH), Harmonic light, Organic materials, hyperpolarizability.

PACS: Nonlinear optics, 42.65.-k, Electric fields, instrumentation for measurement, 07.50.-e, Organic-inorganic hybrid nanostructures, 81.07.Pr, Organic materials optical materials, 42.70.Jk

1. Introduction

Molecular materials for second-order NLO are promising solutions to develop a new generation of low-cost optoelectronic devices [1, 2]. A wide choice of NLO molecule designs has been proposed and synthesized according to well-established molecular engineering rules [3 - 6]. NLO molecules have been also utilized as

molecular markers of biologically active molecules. They help to image targeted structures of cells and membranes by offering multi-photon interactions such as two-photon fluorescence (TPF) [7, 8] or second-harmonic generation (SHG) [9, 10]. In particular, SHG studies provide valuable information about the

symmetry properties of these structures. Combining therapeutic properties with NLO responses helps to localize and characterize the biological sites interacting with drugs and offers a better understanding of the biological processes underlying drugs' therapeutic activity [11]. Analyzing the nonlinear optical properties of the molecule requires knowledge of the quadratic hyperpolarizability coefficient, which controls the nonlinear susceptibility of the second order. Electric Field Induced Second-Harmonic Generation (EFISH) is the predominant and highly effective technique for measuring and characterizing the quadratic hyperpolarizability of NLO polar molecules in solution [12 - 15]. EFISH has been considered the most suitable technique for the screening and development of molecular systems with NLO properties [16]. EFISH can be applied to dipolar and neutral chromophores to measure the scalar product of the dipole moment (μ) and the vector part of the hyperpolarizability tensor (β). It typically displays better signal-to-noise ratios due to the fact that the harmonic emitted light is coherent. The EFISH technique employs a harmonic light scattering (HLS) method for determining the second and third hyperpolarizability orders of organic molecules [17 - 21]. The hyperpolarizability is calculated by measuring $I_{2\omega}$ generated from a chromophore solution under the influence of a strong static electric field E^0 . The solution turns out to be non-centrosymmetric when subjected to the influence combination of an optical laser field E^ω and a static field E^0 . The interaction of the laser beam with the solution produces a coherent second-harmonic (SH) signal. The macroscopic polarization at the SH frequency is defined by [16]:

$$P_i^{2\omega} = \beta_{ijk} E_j^\omega E_k^\omega + \gamma_{ijkl} E_j^\omega E_k^\omega E_l^0 . \quad (1)$$

In this equation, i, j, k, l refer to molecular axes x, y, z , while β_{ijk} and γ_{ijkl} represent the second- and third-order hyperpolarizability tensor components of the molecule, respectively.

The intensity of this harmonic radiation depends on the nonlinear hyperpolarizability β of the sample molecules. In EFISH experiments, the fundamental beam has to be polarized along the direction of the applied field. As a result, the generated second-harmonic will be also polarized along the same direction. The resulting quadratic susceptibility follows this formula [1]:

$$\chi^{(2)} = NF\gamma E_0 \quad (2)$$

where N is the number of molecules per unit volume, F is the local field factor, and γ is the global EFISH hyperpolarizability which is given by [16]:

$$\gamma = \gamma_e + \frac{\mu \cdot \beta}{5kT} \quad (3)$$

where γ_e is a purely electronic cubic contribution and μ is the ground state dipole moment of the molecule, β is the projection of the vectorial component of the tensor of the quadratic hyperpolarizability along the dipole moment axis, and $\mu \cdot \beta / 5kT$ is a quadratic, orientational one.

The molecular factor of merit ($\mu\beta$) value of the investigated chromophore can then be determined from the amplitude and period of the resulting Maker fringes. This determination is possible because the cubic contribution γ_e is often negligible since the contribution of the third-order hyperpolarizability γ_e at 2ω is usually lower than the contribution of the second-order. The need to use a wedge-shaped cell end to measure the intensity of harmonic radiation 2ω as a function of the cell displacement (Fig. 1) is due to the phase shift between the fundamental and harmonic waves into the medium.

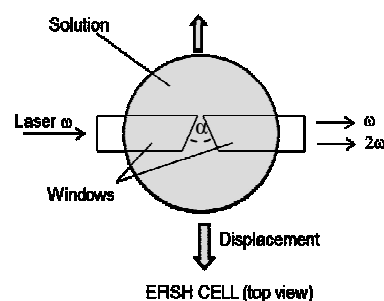


FIG. 1. The EFISH measurement wedge-shaped cell end.

Upon cell translation, the intensity of the second-harmonic radiation is modulated as interference fringes, known as Maker fringes. The width and the periodicity of the fringes are related to the macroscopic susceptibility $\Gamma(x)$ of the solution that depends on $I^{2\omega}$ and on the coherence length $l_c(x)$, according to this relation [22]:

$$\Gamma(x) = \frac{1}{l_c(x)} \cdot \left[A \cdot \sqrt{\frac{I^{2\omega}(x)}{I^{2\omega}(0)}} \frac{E(0)}{E(x)} + B \right] \cdot 10^{-12} \text{ esu} \quad (4)$$

with [13]:

$$l_c(x) = \frac{\pi}{\Delta k} = \frac{\lambda}{4} (n_{2\omega} - n_{\omega}) \text{ or } l_c(x) = \frac{\Delta d}{2} \tan \alpha \quad (5)$$

where $I_{2\omega}(x)$ and $I_{2\omega}(0)$ are the harmonic intensity of solution and the solvent, respectively; $E(x)$ and $E(0)$ are the intensity of the electric field which are applied on solution and the solvent, respectively; A and B are constants depending on the solvent and the windows; Δd is the separation of the fringes minima; finally, α is the angle between the wedged surfaces of the opposite windows (Fig. 1).

The microscopic γ_{EFISH} value can be then calculated from macroscopic susceptibilities of the solvent $\Gamma(0)$ and of the solution $\Gamma(x)$, using the following form [18]:

$$\gamma_{\text{EFISH}} = \frac{M}{\rho \cdot N_a \cdot x \cdot f} [(1+x)\Gamma(x) - \Gamma(0)] \quad (6)$$

where N_a is the Avogadro's number (6.02×10^{23}), M is the molecular weight of the compound, ρ is the density of the solvent, x is the molar fraction of the compound, and f is a local field correction factor introduced to take into account the difference between applied field and field experienced by molecule.

The local field correction factor f can be calculated from the solution refractive indices n_{ω} and $n_{2\omega}$ for the optical fields at ω and 2ω , and

dielectric constants ϵ_{∞} and ϵ of the pure solvent and solution, respectively, according to [13, 16]:

$$f = \left(\frac{n_{\omega}^2 + 2}{3} \right)^2 \frac{n_{2\omega}^2 + 2}{3} \frac{(\epsilon_{\infty} + 2)\epsilon}{\epsilon_{\infty} + 2\epsilon} \quad (7)$$

The $\mu \beta$ value can be then inferred directly from the γ_{EFISH} value using Eq. (3). The ground state dipole moment μ can be measured independently and as a result β can be calculated by EFISH measurement.

In this paper, an optical setup was built and optimized for the EFISH experiment. Hyperpolarizability of some nanostructure organic components of four new organic boron complex molecules and one iodide salt in two different solutions were investigated. The value of merit molecular factor ($\mu\beta$) was calculated for iodide salt which showed a good response to the applied electric field and high-power laser beam.

2. Experimental Setup

In EFISH experiments (Fig. 2), it is important to work in a non-absorbing, or at least weakly absorbing medium, for this reason, a fundamental wavelength of $1.907 \mu\text{m}$ was used, so that the wavelength of its second-harmonic radiation 2ω (i.e. 953.5 nm) is remote from the absorption bands of the studied organic or organo-metallic molecules (generally these bands are not beyond $0.6 - 0.8 \mu\text{m}$ [1]).

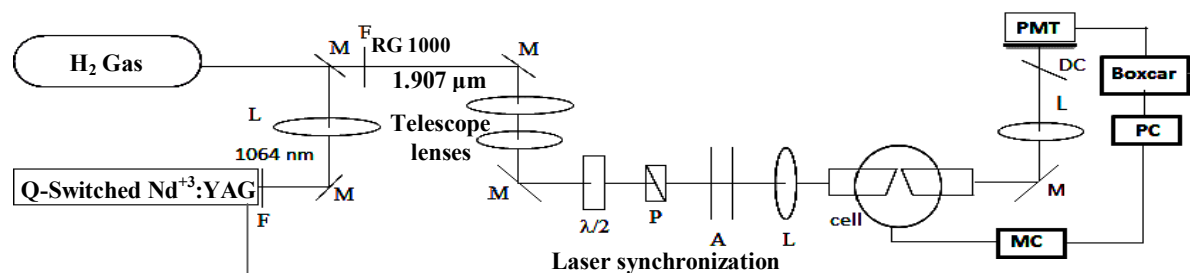


FIG. 2. The schematic diagram of the EFISH experimental setup, where F: Filter; M: Mirrors; L: Lens; $\lambda/2$: Half wave plate; P: Polarizer; A: Attenuator; PMT: Photomultiplier tube; DC: dichroic mirror; MC: Microcontroller; PC: personal computer.

A commercial (SAGA from Thales Laser) 1064 nm Q-switched Nd: YAG nanosecond laser at a 10 Hz repetition rate was used with a hydrogen Raman cell to emit a beam at the required wavelength of $1.907 \mu\text{m}$. The 9 ns pulse duration of the $1.064 \mu\text{m}$ laser beam was focused through a long focal length lens and then reflected by a dichroic mirror (which is HR at $1.064 \mu\text{m}$, HT at $1.9 \mu\text{m}$) into a 50 cm long hydrogen Raman cell of high hydrogen pressure

(55 bar) which shifts the fundamental beam to $\lambda = 1.907 \mu\text{m}$ by stimulated Raman scattering. The backscattered $1.907 \mu\text{m}$ Raman emission with pulse energy of 10 nJ is then passed through the dichroic mirror and a Schott RG 1000 filter is used to filter out any remaining visible light from the laser flash lamp and anti-Stokes emission. Telescope lenses were added to the setup to obtain a collimated beam with a cross-section not to exceed the diameter of the optics.

The polarization of the incident laser beam was controlled by a half-wave plate and a Glan polarizer to ensure normal polarization. The laser power was attenuated by suitable attenuators and then focused into the EFISH cell, which consists of two thick fused quartz windows assembled on a stainless steel holder, using a 20 cm focal length lens. The windows are the most delicate part of the system and can be damaged easily. To avoid damage, the maximum pulse energy incident on the cell should not exceed 3 nJ, while the laser beam should be focused precisely at the center of the cell. For this reason, it was necessary to perform a preliminary alignment using a He-Ne laser and to attenuate the main radiation with filters before accurately focusing

it at the correct position. The inter-electrode distance within the cell measures 2 mm, resulting in a 5 kV pulsed electric field with a width of 200 μs (Fig. 3, left). This electric field is synchronized with the laser pulse. To generate a periodic second-harmonic generation signal, the entire cell is translated perpendicular to the incident beam, producing what is known as Maker fringes (Fig. 3, right). The “poling” field is applied to align molecules and break the statistical centro-symmetry of the solution by the dipolar orientation of solvent and organic molecules. This leads to the generation of two output radiations, the fundamental beam (ω) and a second-harmonic (2ω) when the laser interacts with the sample.

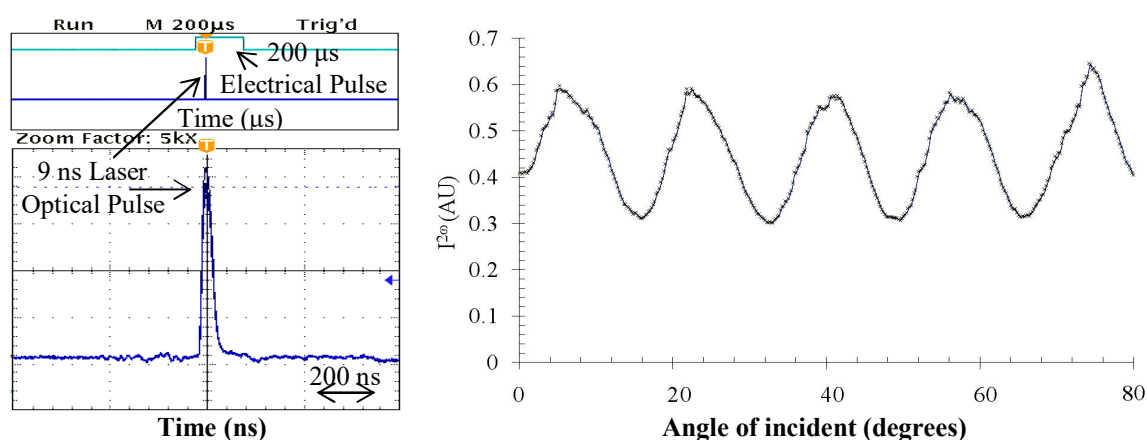


FIG. 3. An example of a SHG signal plotted as a function of the angle of incident of the laser beam.

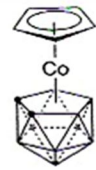
The fundamental radiation was removed by a notch filter, allowing only the second-harmonic radiation to pass through. This second-harmonic radiation was detected by a photomultiplier connected to a high-speed boxcar integrator card and processed by a homemade computer program to calculate the inter-fringe distance and the fringe amplitude. These data were then used to determine the $\mu\beta$ value. In this experiment, two commonly used solvents for β measurements at 1.907 μm , namely dichloromethane (CH_2Cl_2) and chloroform (CHCl_3), were utilized. These solvents have no absorption band for the SH laser light, as reported in the literature. The compounds were dissolved in chloroform or dichloromethane nearly with the same concentrations and poured into the measurement cell which has a volume of 4 ml. For each sample solution measurement, a scan for the pure solvent was first performed, and then the compound solution was measured to calculate the inter-fringe and the fringe

amplitudes. The measurements of solvent and sample solution were repeated five times, to minimize possible errors due to the decrease of the incident radiation energy during the measurements. Subsequently, the average amplitude values obtained from these repetitions were used to calculate the $\mu\beta$ value. The cell was carefully washed after each scan (it is possible to use any solvent, but it is necessary to clean the cell with CH_2Cl_2 before the new measurement) and dried with compressed air.

3. Results

Maker fringes were investigated for different types of organic molecules (supplied by the Chemistry Department at Catania University, Italy) dissolved in CF (chloroform, CHCl_3) or in DCM, (dichloromethane, CH_2Cl_2). Names, properties, concentration, and measured marker fringes of these solutions (Figs. 4 - 8) are as follows:

a) Nepla Carbo - nona Boro - hexadeca Hydro - Cobalt, $\text{CoC}_7\text{B}_9\text{H}_{16}$:

Colour	Molecular Weight (g/mol)	N_s (mmol/L)	Molecular structure
Yellow	256.43	5.34	

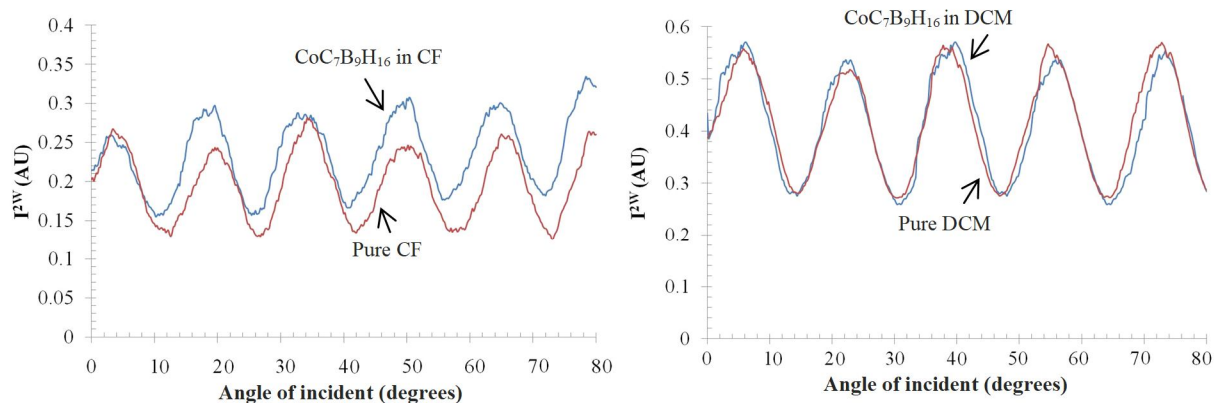
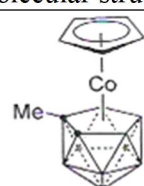


FIG. 4. Maker fringes of $\text{CoC}_7\text{B}_9\text{H}_{16}$ in CF (right) or in DCM (left) and the pure solvent.

b) Octo Carbo - nona Boro - octadeca Hydro - Cobalt, $\text{CoC}_8\text{B}_9\text{H}_{18}$:

Colour	Molecular Weight (g/mol)	N_s (mmol/L)	Molecular structure
Yellow	270.46	5.15	

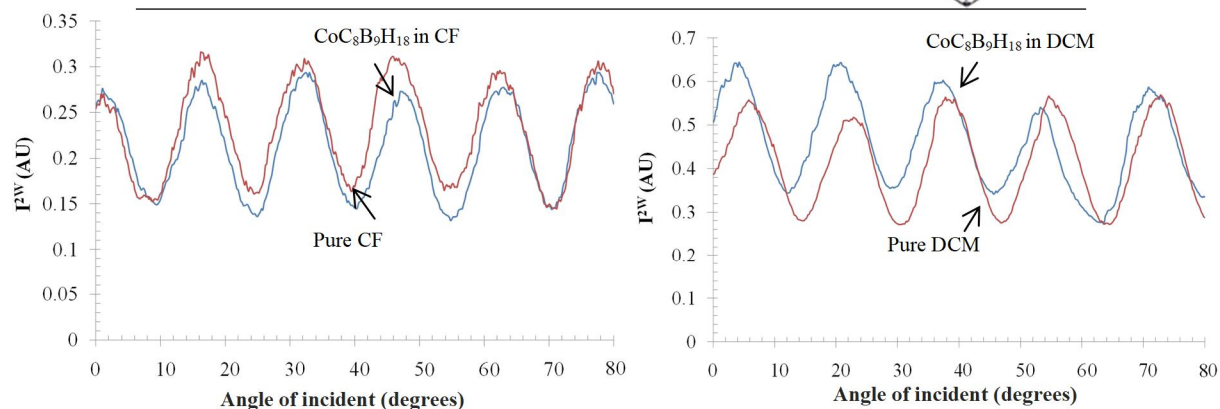
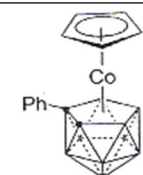


FIG. 5. Maker fringes of $\text{CoC}_8\text{B}_9\text{H}_{18}$ in CF (right) or in DCM (left) and the pure solvent.

c) Trideca Carbo - nona Boro - eozan Hydro - Cobalt, $\text{CoC}_{13}\text{B}_9\text{H}_{20}$:

Colour	Molecular Weight (g/mol)	N_s (mmol/L)	Molecular structure
Dark Yellow	332.53	5.27	

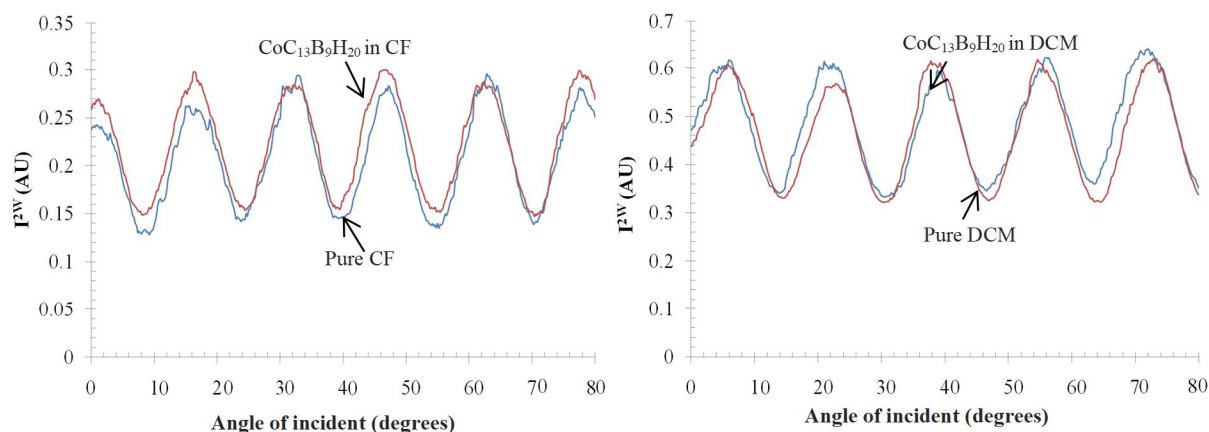


FIG. 6. Maker fringes of $\text{CoC}_{13}\text{B}_9\text{H}_{20}$ in CF (right) or in DCM (left) and the pure solvent.

d) Trideca Carbo - octa Boro - doecozan Hydro - dicobalt, $\text{Co}_2\text{C}_{13}\text{B}_8\text{H}_{22}$:

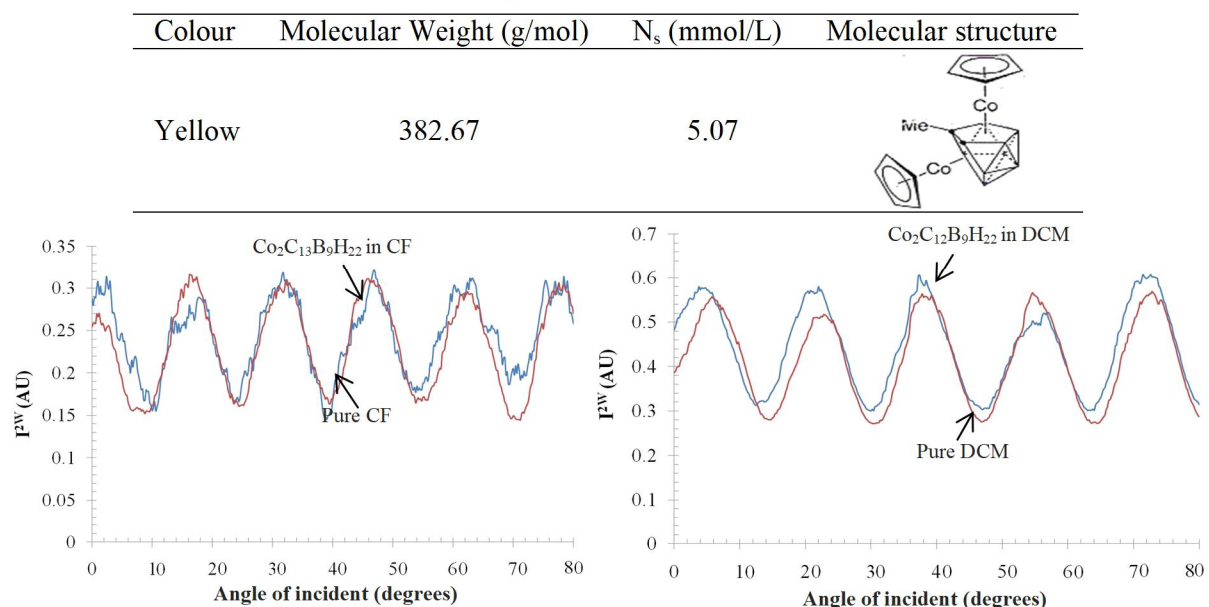


FIG. 7. Maker fringes of $\text{Co}_2\text{C}_{13}\text{B}_9\text{H}_{22}$ in CF (right) or in DCM (left) and the pure solvent.

e) (2-(2-[5'-(N,N-dimethylamino)-(2,2'-bithiophen)-5-yl]vinyl)-1-methylquinolin-1-ium iodide):

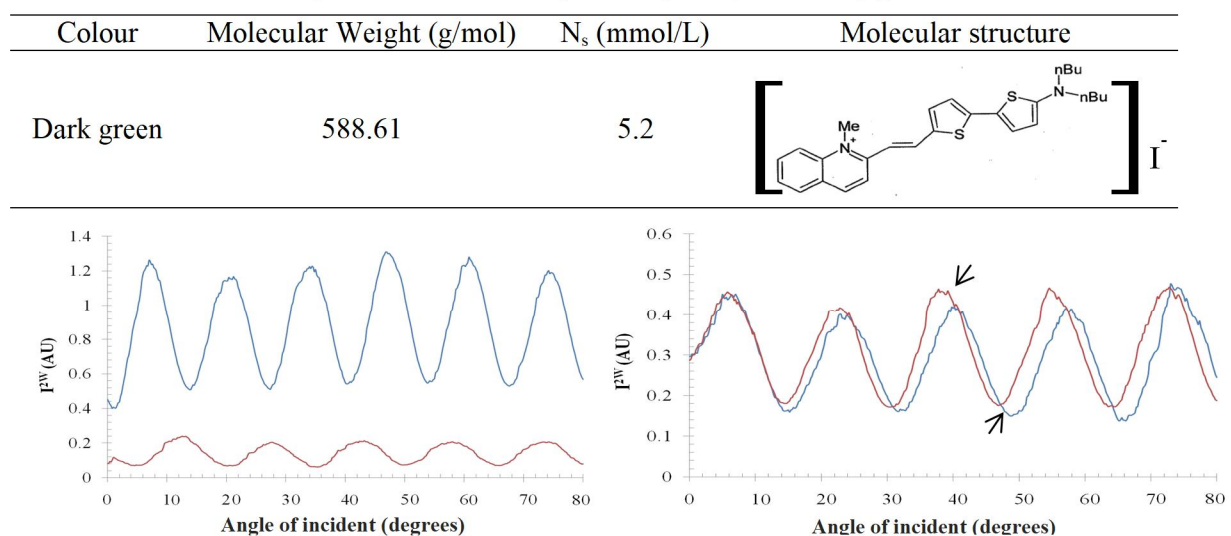


FIG. 8. Maker fringes of Iodide salt in CF (right) or in DCM (left) and the pure solvent.

4. Discussion and Calculations

Results of organic boron complexes that were dissolved in either CF or DCM demonstrated no significant changes in Maker fringes in comparison with pure solvent. This means that molecules are not polarizable or, thus other techniques such as Hyper-Rayleigh light scattering, have to be applied to measure the value of the hyperpolarizability β [23 - 24]. On the contrary, the iodides salt, (2-(2-[5'-(N,N-dimethylamino)-(2,2'-bithiophen)-5-yl]vinyl)-1-methyquinolin-1-ium-iodide), showed a good response only when dissolved in a low dipole moment polar CF comparing with the same amount of salt dissolved in a higher dipole moment polar DCM. This difference in response could likely be attributed to the molecular structure of the solvents. In CF, the three chlorine atoms are at the bottom three points of a tetrahedron. Thus the x and y components of the individual C-Cl bond dipoles cancel, leaving

only the z component, while for dichloromethane (DCM), the y components fully cancel, but the x components do not. However, the harmonic output in the EFISH cell arises only from the discontinuities area between two glass windows along the z-axis [13]. In this case, the second-order nonlinear hyperpolarizability β is equal to $\beta_{zxx} + \beta_{zyy} + \beta_{zzz}$ and has a significant value if the molecules of the solution have a considerable dipole moment along the z-axis [13] as in salts dissolved with CF solvent. The significant Maker changes in fringes between the iodine salt solution and its pure solvent (CF) make it possible to calculate the value of the hyperpolarizability for the sample with the aid of the local software that was attached to the experiments. For used parameters (i. e. mass weighed: 23.6 mg; volume: 8 ml; molar mass 588.61 g.mol⁻¹; solvent: chloroform; inter-fringe medium 1522.80; average intensity: 0.1544) the results are:

2-(2-[5'-(N,N-dimethylamino)-(2,2'-bithiophen)-5-yl]vinyl)-1-methyquinolin-1-ium-iodide				
$\Gamma(x)$ (10 ⁻¹⁴ esu)	$\gamma_{(EFISH)}$ (10 ⁻³⁴ esu)	$\mu\beta$ (10 ⁻⁴⁸ esu)	μ (10 ⁻¹⁸ esu)	β (10 ⁻³⁰ esu)
15.12 ± 0.72	65.02 ± 5.37	1320 ± 15	3.52 ± 0.3	375 ± 6

The previous values are not yet calculated theoretically to compare them with the modeling methods of quantum chemistry but their order of magnitude can be checked by comparing them with other published organic components [25 - 27]. The $\mu\beta$ value of the studied iodide salt in this paper displays a higher value in comparison with the values that have already been obtained for other iodide salts, which were up to 1200×10^{-48} esu [25]. The significantly higher value of $\mu\beta$ of the studied iodide salt might make it attractive to many applications. Unfortunately, the amount of supplied tested samples was too little and not enough to do further study of hyperpolarizability values for the sample as a function of solution concentration. However, the results obtained from this optimized optical setup show that iodide salts presented here have good nonlinear properties perhaps due to the increase in the conjugated interconnect length band that enhances the optical nonlinearity [28].

investigate the coefficients of quadratic hyperpolarizability (which is a property of the nonlinear optical second order) of nonlinear organic molecules pumped using the method called "Maker fringes". Four organic boron complex molecules were studied in two different solvents and showed no significant changes in Maker fringes in comparison with pure organic solvent. Thus, no quadratic hyperpolarizability coefficients can be calculated for boron complex molecules using this method. On the contrary, the studied iodide salt showed a significant change in Maker fringes when dissolved in CF polar solvent. The merit molecular factor ($\mu\beta$) value of the investigated iodide salt was calculated and was found to be $(1320 \pm 15) \times 10^{-48}$ esu which is considered a relatively good value in comparison with other studied components in some references. This means that the studied iodide salt molecules have a good dipole moment, which makes it an excellent candidate for different nonlinear applications.

5. Conclusion

An optimized optical setup with 10 nJ pulse energy of 1.907 μ m laser was arranged to

References

- [1] Zyss, J., "Molecular Nonlinear Optics: Materials Physics and Devices", (Academic Press, Boston, 1994).
- [2] Shi, Y., Lin, W., Olson, D.J., Bechtel, J.H., Zhang, H., Steier, W.H., Zhang, C. and Dalton, L.R., *Appl. Phys. Lett.*, 77 (1) (2000) 1.
- [3] Jang, S-H. and Jen, A. K-Y., "Introduction to Organic Electronic and Optoelectronic Materials and Devices". Eds. S.-Sh. Sun and R. Larry, (CRC Press, Dalton, 2008), p467.
- [4] Nalwa, H.S. and Miyata, S., "Nonlinear Optics of Organic Molecules and Polymers", (CRC Press, New York, 1997).
- [5] Verbiest, T., Houbrechts, S., Kauranen, M., Clays, K. and Persoons, A., *J. Mater. Chem.*, 7 (1997) 2175.
- [6] Reeve, J.E., Collins, H.A., Mey, K.D., Kohl, M.M., Thorley, K.J., Paulsen, O., Clays, K. and Anderson, H.L., *J. Am. Chem. Soc.*, 131 (2009) 2758.
- [7] Denk, W., Strickler J.H. and Webb, W.W., *Science*, 248 (1990) 73.
- [8] Cesaretti, A., Foggi, P., Fortuna, C.G., Elisei, F., Spalletti, A. and Carlotti, B., *J. Phys. Chem. C*, 124 (2020) 15739.
- [9] Moreaux, L., Sandre, O., Blanchard-Desce, M. and Mertz, J. *Opt. Lett.*, 25 (2000) 320.
- [10] Chen, S., Fai Li, K., Li, G., Wai Cheah, K. and Zhang, Sh., *Light-Sci. Appl.*, 8 (17) (2019) 1.
- [11] Yan, P., Millard, A.C., Wei, M. and Loew, L.M., *J. Am. Chem.*, 128 (34) (2006) 11030.
- [12] Oudar, J.L. and Chemla. D.S., *J. Chem. Phys.*, 66 (1977) 2664.
- [13] Levine, B.F. and Bethea, C.G., *Chem. Phys.*, 63 (1975) 2666.
- [14] Kajzar, F., Ledoux, I. and Zyss, J., *J. Phys. Rev. A*, 36 (1987) 2210.
- [15] Ghanavatkar, C.W., Mishra, V.R. and Sekar, N., *Dyes Pigments*, 191 (2021) 109367.
- [16] Oudar, J.L., *J. of Chem. Phys.*, 67 (2) (1977) 446.
- [17] Maker, P.D., *Phys. Rev. A*, 1 (1970) 923.
- [18] Dragonetti, C., Colombo, A., Marinotto, D., Righetto, S., Roberto, D., Valore, A., Escadeillas, M., Guerchais, V., Le Bozec, H., Boucekkine, A. and Latouche, C., *J. Organomet. Chem.*, 751 (2014) 1.
- [19] Achellea, S., Kahlalb, S., Barsellac, A., Saillardb, J-Y., Cheb, X., Valletb, J., Burešd, F., Caroa, B. and Guena, F.R., *Dyes Pigments*, 113 (2015) 562.
- [20] Colombo, A., Dragonetti, C., Marinotto, D., Righetto, S., Griffini, G., Turri, S., Akdas-Kilig, H., Fillaut, J., Amar, A., Boucekkine, A. and Katane, C., *Dalton Trans.*, 45 (2016) 11052.
- [21] Di Carlo, G., Pizzotti, M., Righetto, S., Forni, A. and Tessore, F., *Inorg. Chem.*, 59 (2020) 7561.
- [22] Singh, A., "École normale supérieure de Cachan - ENS Cachan", (2012) p.70.
- [23] Noordman, O.F.J. and Van Hulst, N.F., *Chem. Phys. Lett.*, 253 (1996) 145.
- [24] Wang, C.H., Lin, Y.C., Tai, O.Y. and Jen, A.K.Y., *J. Chem. Phys.*, 119 (12) (2003) 6237.
- [25] Fortuna, C.G., Bonaccorso, C., Qamar, F., Anu, A., Ledoux, I. and Musumarra, G., *Org. Biomol. Chem*, 9 (2011) 1608.
- [26] Choa, M.J., Choia, D.H., Sullivanb, P.A., Akelaitis, A.J.P. and Dalton, L.R., *Prog. Polym. Sci.*, 33 (2008) 1013.
- [27] Dalton, L.R., Sullivan, P.A. and Bale, D.H., *Chem. Rev.*, 110 (1) (2010) 25.
- [28] Delower, M., Bhuiyana, H., Ashrafa, M., Teshomeb, A., Graeme Gainsforda, J., Kaya, A.J., Asselberghsb, I. and Claysb, K., *Dyes Pigments*, 89 (2) (2011) 177.