International Journal of Engineering Research & Management Technology
(Peer-Reviewed, Open Access, Fully Refereed International Journal) ISSN: 2348-4039
Volume 11, Issue-4 July-August- 2024 Impact Factor: 7.09
Email: editor@ijermt.org www.ijermt.org

REVIEW ON USE OF VARIOUS ORGANIC DYES IN INORGANIC MATERIALS FOR APPLICATION OF NON LINEAR OPTICAL DEVICES

Sanchita Ajay Borkar
Research scholar, Department of physics
Deogiri College Aurangabad

Dr.Anil N.Ardad
Associate Professor, Department of physics
Deogiri College Aurangabad

Abstract

Enhancing non-linear optical (NLO) device performance can be achieved by integrating organic dyes into inorganic materials. This review emphasizes the synthesis, structural attributes, and optical properties of various organic dyes embedded in inorganic matrices to improve NLO qualities. Embedding dyes such as rhodamine, fluorescein, and stilbene derivatives into hosts like silica, titania, or zeolites results in significantly enhanced non-linear optical responses. The synergy between the electrical properties of organic dyes and the mechanical strength and stability of inorganic matrices creates materials with superior second-order and third-order non-linearities, which are crucial for optical switching, modulation, and frequency conversion applications.

The review explores several methods for producing these hybrid materials, including sol-gel processes, in situ polymerization, and surface modification techniques. It highlights that the performance of NLO materials depends on the orientation, concentration, and distribution of dyes within the inorganic matrix. Advances in computer modeling have shed light on molecular interactions and energy transfer mechanisms at the organic-inorganic interface, aiding in the design of next-generation NLO materials. Additionally, the review addresses the environmental compatibility, stability, and durability of these hybrid systems, which are critical for their practical application in optical devices.

Future research directions include identifying new inorganic hosts to enhance device performance and developing novel organic dyes with tailored non-linear optical properties. By combining experimental findings with theoretical insights, this study provides a comprehensive perspective on the current state and future prospects of organic dye-doped inorganic materials in the realm of non-linear optics.

Keywords:*Various organic dyes, inorganicmaterials,non linear optical devices*

Introduction

Non-linear optical (NLO) materials are essential for advanced photonic applications, including optical switching, modulation, frequency conversion, and data processing. These applications rely on the non-linear optical response of a material, which is determined by the interaction between intense light and the material, leading to phenomena such as second-harmonic generation (SHG), third-harmonic generation

(THG), and two-photon absorption. Historically, inorganic materials like lithium niobate, potassium titanyl phosphate, and barium borate have been widely used for NLO applications due to their exceptional optical properties and stability.

However, the need for materials with higher NLO coefficients, faster response times, and greater manufacturing flexibility has driven researchers to explore organic dyes as potential alternatives. Organic dyes, such as rhodamine, fluorescein, and stilbene derivatives, exhibit large molecular hyperpolarizabilities, which enhance NLO responses. Incorporating these dyes into inorganic matrices results in hybrid materials with superior NLO performance.

The advantageous electrical characteristics of organic dyes combined with the mechanical strength and thermal stability of inorganic hosts create hybrid materials with enhanced non-linear optical (NLO) performance. There are several benefits to incorporating organic dyes into inorganic materials. First, the inorganic matrix provides a robust environment that protects the dye molecules from photodegradation and thermal decomposition, thereby increasing the longevity of NLO devices. Second, the inorganic host can be designed to control the distribution and orientation of the dye molecules, optimizing the NLO response. This optimization can be achieved through various techniques.Additionally, hybrid materials can be manufactured using methods such as sol-gel processes, in situ polymerization, and surface modification, enabling flexible and scalable production. This paper aims to provide a comprehensive overview of the use of organic dyes in inorganic matrices for NLO applications. It will explore the types of organic dyes typically used, the selection of inorganic hosts, and the synthesis techniques employed to produce hybrid materials. Furthermore, the paper will examine the optical properties and performance metrics of these materials, with a particular focus on the factors that influence their NLO behavior.

The study also highlights the potential and challenges of these materials in developing next-generation NLO devices by examining recent research and technological advancements. The following sections will cover the fundamental concepts of non-linear optics, the properties of organic dyes, and the methods for embedding these dyes into inorganic matrices. This study aims to provide insights into the current state of research and inspire further investigations into the design and application of organic dye-doped inorganic NLO materials. By illustrating practical applications and recent improvements, achievement of both objectives will be undertaken.

OBJECTIVE

1. To study use of various organic dyes in inorganic materials
2. To study use of various organic dyes for application of non-linear optical devices

Nonlinear Optical Materials: Best Practices:

Currently, there is a wide range of inorganic non-linear optical materials available, each with unique wavelengths, damage thresholds, and optical characteristics. The aim of this study is to develop materials that can meet all necessary criteria, including faster response times, high laser damage thresholds, and a broad transparency range, while also offering flexibility, ease of processing, and compatibility with other materials. The demand for nonlinear optical materials is expected to grow significantly due to the increasing need for high-bandwidth fiber optic networks and high-speed optical computing.

New Initiatives:

On the other hand, the study that was presented at the ACS conference in 1982 gave the organic nonlinear optical material investigations a boost of forward momentum. In the time since then, the research has begun to become more significant. Organic compounds with delocalized conjugated electrons were discovered. These compounds exhibit outstanding nonlinear optical properties and high-speed responsiveness due to the high mobility of electrons. Therefore, these compounds were discovered. As it was mentioned that the 21st century would be the age of photonics. Among the key technologies in this field, advancing wavefront control through the use of organic nonlinear optical effects is considered highly significant.Research and development on organic materials that possess outstanding nonlinear optical characteristics, as well as intensive practical research, have been carried out at this time.

Recent advancements in material chemistry indicate that, although inorganic materials remain the preferred choice for many devices, there is growing interest in organic materials due to their adaptability to various applications. Organic molecules present exciting opportunities for material researchers to design custom-tailored materials with properties at both the macroscopic and microscopic levels that closely reflect the modeled or actual behavior of individual molecules. Over the past two decades, the field of organic molecular materials has revolutionized material usage in the modern world. The development of novel functional organic materials is rapidly expanding, and these materials are likely to replace traditional ones with more cost-effective and efficient alternatives while enabling new applications.Considering the technological applications of organic materials, the current research focus on five technical areas: (1) structural and multifunctional materials; (2) energy and power materials; (3) photonic and electronic materials; (4) functional organic and hybrid materials; and (5) bioderived and bio-inspired materials. These areas are prioritized based on their significance in the field of organic materials. This work focuses on "PHOTONIC MATERIALS," one of the five primary technical thrust areas in organic materials. These materials have potential applications in linear and electric non-linear optics, also known as photonics. Organic non-linear optical materials offer several advantages, including the following.:

- Easy to process: When compared to inorganic optical materials, these materials are simpler to process. This is due to the fact that they do not require the use of electric poling or the fabrication of big single crystals.
- Lower cost: A reduced cost of fabrication is directly proportional to the ease with which the material may be processed.
- High second- and third-order susceptibility: This technique demonstrates remarkable performance in terms of doubling and tripling the frequency of light that passes through it, which places it on par with inorganic materials at the very least.
- High electro-optic coefficient: When it comes to electro-optic modulation for high-speed devices, materials that have a high electro-optic coefficient are more suited.
- Colorless: It is thought that the transparency of the material that is being doubled will prevent the absorption of visible light, which will make it possible to double a wide range of light frequencies.

- Resistant to laser damage: This makes the tripled material an excellent candidate for use in photonic applications since it is able to withstand exposure to 432,000 pulses of 20 nanoseconds each at a frequency of 20 hertz without causing any harm to the organic material.

Next Practices:

Despite the fact that organic materials and dyes exhibiting exceptional nonlinear optical properties are currently considered best practices in photonics technology, these organic materials still face challenges similar to those encountered with inorganic materials. These challenges include significant light-induced degradation or bleaching and aggregation at higher dye concentrations. To address these issues and enable the effective use of highly nonlinear dyes, the strategy of doping dye molecules into a polymer matrix is proposed. This approach, known as dye-doped polymer matrix material, has the potential to enhance both the concentration of absorptive or fluorescence centers and the optochemical and optophysical stability of the material.

This strategy highlights the advantages of dye-doped polymer nonlinear materials compared to both organic and inorganic nonlinear materials for advancing future photonics technology. To illustrate these points, this is considered an example involving an organic dye, 4-[4-(Dimethylamino)styryl]. The polymer matrix used is polymethyl methacrylate methacrylic acid (PMMA-MA), which includes -1-docosyl pyridinium bromide. The nonlinear properties of the novel dye, designated as 4-[4-(Dimethylamino)styryl], are explored, focusing on its two-photon generated fluorescence and optical limiting capability, both in solution form (chloroform) and within the PMMA-MA matrix with -1-docosyl pyridinium bromide, referred to as DASPB.

The study investigated the linear absorption, single-photon fluorescence, and two-photon induced fluorescence behavior of this dye. Using a picosecond laser beam, the intensity-dependent nonlinear absorption across various wavelengths and the optical limiting behavior are analyzed.

A novel functional microemulsion system for ultra-precision chemical-mechanical polishing (CMP) of KDP crystals was developed. This system, referred to as KH_2PO_4 (KDP) aqueous solution-in-oil (KDP aq/O), operates at room temperature and comprises decanol, Triton X-100, and an aqueous solution of KH_2PO_4. The KDP aq/O microemulsion system was extensively studied and applied as a polishing solution in KDP CMP technology. The proposed approach utilizes the KDP aq/O microemulsion for KDP polishing through a controlled deliquescent mechanism.

In this system, the micelles contain the KDP aqueous solution, which acts as the chemical etchant in the polishing process. This setup ensures that the reaction between the KDP crystal and the KDP aqueous solution occurs only when the microemulsion undergoes deformation due to an external force. The conventional water-in-oil (W/O) microemulsion was modified by replacing water with KDP aqueous solutions of varying concentrations (cKDP), based on interface reaction dynamics. The effectiveness of the controlled deliquescent mechanism was demonstrated by a decrease in the material removal rate (MRR) as the cKDP increased, which helped reduce corrosion pits on the KDP surface.

Moreover, KDP polished with the KDP aq/O microemulsion (with cKDP adjusted from 10 mM to 100 mM) exhibited a rougher surface compared to those polished with the W/O microemulsion. However, due

to the optimal deliquescent rate and MRR, the lowest surface root-mean-square roughness of 1.5 nm was achieved with a 30 mmol/L KDP aqueous solution.

Methodology

To develop nanomolecules that incorporate organic dyes into inorganic materials for nonlinear optical (NLO) device applications, several critical steps must be followed. The first step involves selecting suitable organic dyes with strong NLO properties, such as high second-order or third-order susceptibility. Common examples include stilbenes, porphyrins, and phthalocyanines, known for their exceptional optical qualities.

The next step involves choosing appropriate inorganic host materials, such as silica, titania, or zeolites, due to their stability, transparency, and ability to effectively disperse dye molecules. The synthesis typically begins with the preparation of the inorganic matrix, which can be achieved through sol-gel methods or hydrothermal processing. This ensures the formation of a porous structure capable of accommodating the organic dye molecules.Subsequently, the organic dyes are incorporated into the inorganic matrix. This can be achieved through covalent bonding, where functional groups on the dye molecules form stable connections with the inorganic host, or through physical encapsulation, where dyes are trapped within the pores of the matrix during synthesis.

Characterizing the nanocomposites is crucial to ensure effective integration and optimal NLO performance. Various techniques are employed to analyze the morphology and structure of the nanomaterials, including scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD). Spectroscopic techniques such as ultraviolet-visible (UV-Vis), fluorescence, and Raman spectroscopy are used to examine the optical properties and confirm the presence and dispersion of organic dyes within the inorganic matrix.

To evaluate the nonlinear optical properties of the produced nanocomposites, techniques such as Z-scan and degenerate four-wave mixing are employed. These methods measure parameters such as the nonlinear refractive index and absorption coefficient. The effectiveness of the nanocomposites in NLO devices can be assessed using these measurements, which helps determine their potential applications. Optimization of synthesis parameters, dye concentration, and matrix composition is performed to enhance the performance of NLO devices, paving the way for advancements in optical switching, signal processing, and telecommunications.

Case study

Sample Preparation

Aldrich Chemical Company's DASPB, which is available commercially, undergoes purification through two recrystallization steps using spectrograde ethanol, followed by vacuum sublimation. Spectroscopy is employed to assess its purity. Purified chloroform is used as the solvent. A polymer matrix composed of polymethyl methacrylate (PMMA) and methacrylic acid (MA) is used in the film preparation process. The

hot press method is employed to create thin films of DASPB doped with PMMA-MA. Thin films of varying thicknesses can be produced by sandwiching two glass slides together.

Linear Optical Properties of DASPB

The molecular structure of DASPB is illustrated in Figure 1. A charge transfer between the aromatic moiety, serving as the electron donor, and the bromine unit, acting as the electron acceptor, can be proposed to explain the high $\chi 3$ value detected using the Z-scan technique. The linear absorption spectra of DASPB in chloroform are measured using a VARIAN Cary UV-vis-IR recording spectrophotometer. This measurement is performed with a quartz cuvette having a path length of one centimeter, and the cuvette is doped with a polymethyl methacrylate methacrylic acid (PMMA-MA) film.

Figure 2 shows the linear absorption spectra of DASPB in chloroform at a solute concentration of d0 = 0.0001 mol/L. This spectrum excludes the impact of the solvent. The absorption spectrum features a strong band with peak absorption at 478 nm and a bandwidth of 100 nm, a medium absorption peak at 270 nm with a bandwidth of 80 nm, and no linear absorption observed in the spectral range from 580 to 2000 nm, except for infrared absorption between 1200 nm and 1600 nm, as demonstrated by the spectral curve.

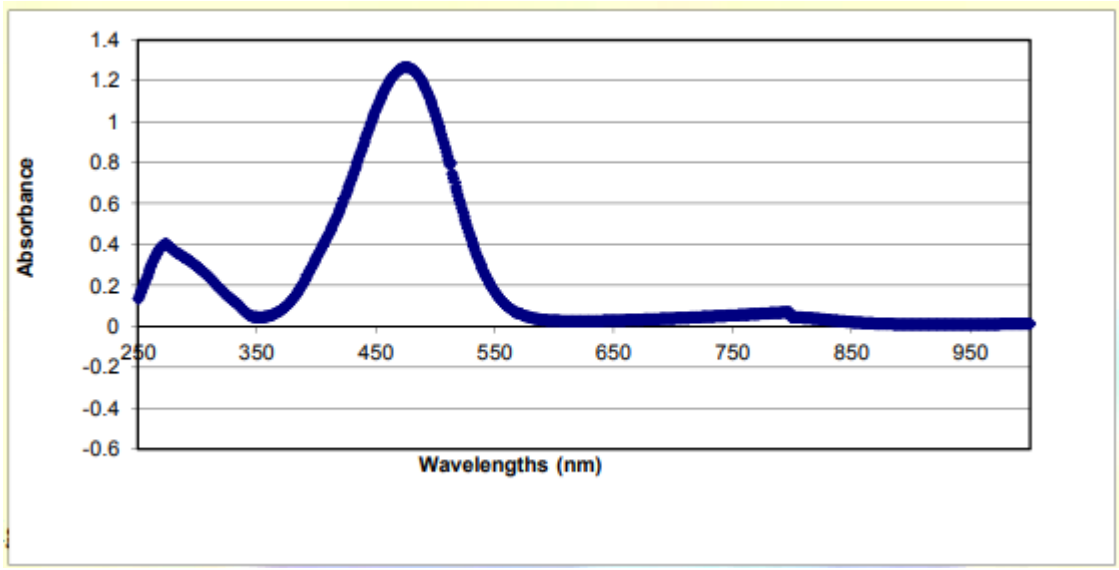

Figure 1: DASPB's molecular shape and structure

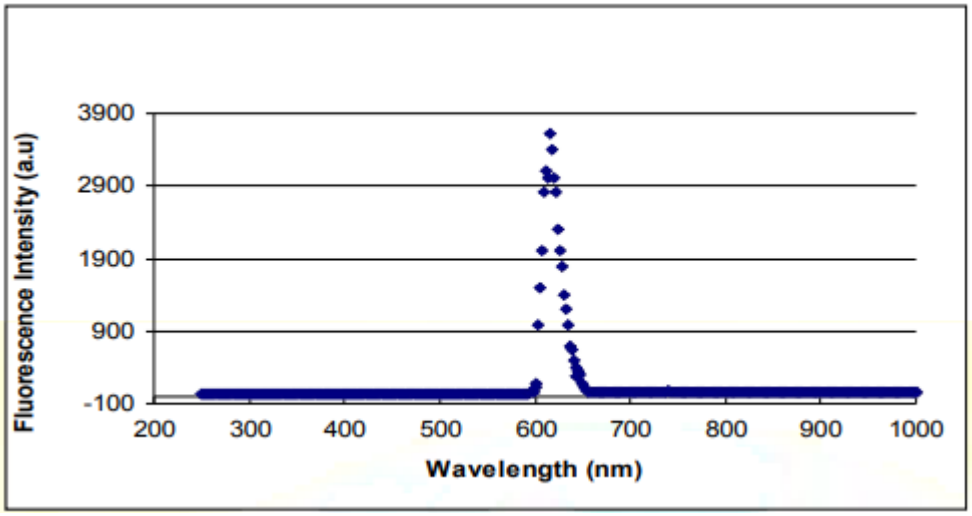

Figure 2 :Irradiation at 532 nm caused fluorescence to be generated by a single photon.

Utilizing a spectral fluophotometer (Rf 50000U from Schmadza) with a spectral resolution of 1 nm, the single photon fluorescence spectrum of the sample is measured for a 1 cm –path DASPB in chloroform with the solute concentration of 0.0001 mol/L. This is done in order to determine the concentration of the solute. With a bandwidth of sixty nanometers, the single-photon produced fluorescence had a peak wavelength of 610 nanometers (Figure 1). An example of a single photon fluorescence is shown in Figure 2, which was obtained by using a Nd:YAG laser beam to excite DASPB at a wavelength of 532 nm.

NONLINEAR OPTICAL PROPERTIES

The absorption spectrum of DASPB demonstrates that there is no linear absorption over the whole spectral range, which ranges from 580 to 1800 nanometers. The only exception to this is the fact that the DSAPB solution absorbs a significant amount of infrared light between 1,200 and 1,600 nanometers. When this dye is exposed to near-infrared and infrared laser beams with wavelengths larger than 700 nm, it has been demonstrated that it demonstrates a frequency upconversion fluorescence that is much higher than average. All of this speaks to the likelihood that a TPA process that is quite strong is taking place inside the sample.

Two-photon Excited Fluorescence Emission

Figure 3 depicts the TPA-induced emission spectra of 0.0005 mol/L DASPB in chloroform with a route length of 1 cm stimulated with a laser beam with a wavelength of 1064 nm. For the purpose of determining the upconversion efficiency, VIS cutting filters were utilized to reduce the amount of energy that was communicated by the pump. On the basis of a comparison with Figure 2, it is evident that the TPA-induced emission spectrum of DASPB with a significantly higher concentration exhibits a red shift in comparison to the single photon absorption analysis conducted with a significantly lower

concentration. Reabsorption of dye pigment is one possible explanation for this phenomenon.

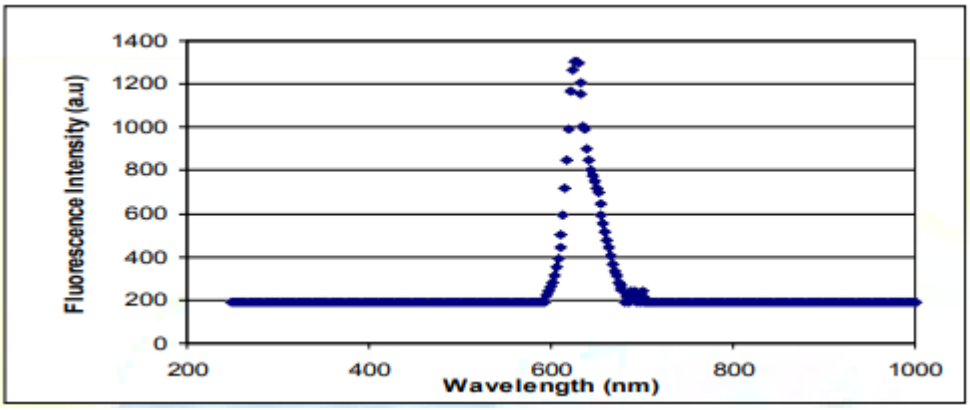

Figure 3 : Two-photon induced emission spectrum of DASPB at 1.06 µm irradiation.

In order to investigate the nonlinear optical characteristics of the sample, the Z-scan approach is frequently utilized. A single beam is tightly focused onto a thin nonlinear medium this is the Zscan technique is all about. It is possible to determine the nonlinear refractive index n2 by measuring the transmittance via a tiny aperture in the far field due to the fact that this measurement is made. The measurement of the transmittance enables the estimation of the two-photon absorption coefficient β. This is accomplished by eliminating the aperture. The experimental setup for the measurement of nonlinear absorption is depicted. This configuration includes saturation absorption in the linear absorbing area as well as two-photon absorption in the transmitting section of the DASPB. Although the system is insensitive to nonlinear refraction when it is configured with an open aperture (S=1), it is nevertheless capable of measuring the nonlinear absorption cross section at this configuration. It is anticipated that a Z-scan trace that does not contain an aperture will be symmetric with regard to the focus (Z = 0), which is the point at which the least transmittance (for example, multiphoton absorption) or the greatest transmittance (for example, saturation of absorption) takes place. There is a straightforward method for calculating the nonlinear coefficient using the Z-scan transmittance curve. Picosecond laser beams (32 picoseconds, 10 hertz) and nanosecond laser beams (six nanoseconds, 20 hertz) are utilized in order to investigate the behavior of DASPB in its linear absorptive region. These beams originate from the second harmonic of a Q-switched, mode-locked Nd:YAG laser system and are operating at 532 nanometers.

CONCLUSION

Incorporating organic dyes into inorganic materials for nonlinear optical (NLO) device applications represents a promising strategy with significant potential to enhance the functionality and performance of these devices. By leveraging the unique optical properties of organic dyes alongside the stability and versatility of inorganic matrices, it is possible to construct nanocomposites with outstanding NLO characteristics. The precise control over the material's structural and optical properties is facilitated through the careful selection of organic dyes and inorganic hosts, coupled with advanced synthesis techniques.Characterization via various spectroscopic and microscopic methods ensures the efficient integration and uniform distribution of dyes within the matrix. Additionally, comprehensive examination of the NLO properties confirms the practical applicability of these dyes. This multidisciplinary approach not only advances the field of nonlinear optical materials but also paves the way for the development of

efficient optical devices for use in telecommunications, signal processing, and other high-tech applications.

REFRENCESS

[1] Shubrajyotsna Aithal, Sreeramana Aithal and Gopalkrishna Bhat, 2012, Phase Conjugation in Two Photon Absorbing Dye films by Degenerate Four-wave Mixing, 3rd International Conference on Photonics 2012, Penang, Malaysia. Published in IEEEXplore ISBN: 978-1-4673-1463-3, pp - 235-239.

[2] Shubrajyotsna Aithal, P. S. Aithal, and Gopalkrishna Bhat, 2012, Study of Degenerate Four-Wave Mixing in Disperse Orange Dye-doped Polymer Film, Advanced Materials Research Journal, Trans Tech Publications (TTP), Switzerland, 584 pp 526-530.

[3] Shubrajyotsna Aithal, Aithal P.S., and Gopalkrishna Bhat, 2014, Degenerate four-wave mixing in DASPB dye-doped polymer film, published in Part IV Quantum Optics, Chapter 12, Advances in Laser Physics and Technology, Edited by Man Mohan, Anil Kumar Maini, Aranya A. Bhattacherjee and Anil K. Razdan under the imprint of Foundation Books, Cambridge University Press India Pvt Ltd. pp 179 - 195, ISBN: 978-93-844634-1-0.

[4] Shubhrajyotsna Aithal, Sreeramana Aithal and Gopala Krishna Bhat, 2016, Study of Optical Limiting and Optical Phase Conjugation in DASPB dye-doped polymer films, GSTF Journal of Physics and Applications (JPA) 1 (1), pp. 34-39.

[5] Shubhrajyotsna Aithal, Aithal P. S., and Bhat G. K., 2015, Comparative Study on Azo dye-doped Polymer Films for Optical Phase Conjugation, International Journal of Science and Research, 4 (4), pp 436 – 441.

[6] Swalen J. D. and Kajzar F., 2019, Nonlinear absorption in optical limiting, Nonlinear Optics, 27, pp 13-32.

[7] Tanaka H., Horikoshi A., Fujiwara H., and Nakagawa K., 2018, Phase conjugation in saturable absorbing dye films by degenerate four-wave mixing and holographic processes, Optical Review 9 (3) pp 106-111.

[8] Van Stryland E. and Chase L.L., 2015, Two-Photon Absorption: inorganic materials", in Handbook of Laser Science and Technology; supplement 2: Optical Materials, section 8, pp 299-326, Ed. M. Weber, CRC Press.

[9] Wei T. H., Hagan D. J., Van Stryland E. W., Perry J. W., and Coulter D. R., 2020, Direct Measurements of Nonlinear Absorption and Refraction in Solutions of Pthalocyanines, Appl. Phys. B54, pp 46.

[10] Yariv A., 2021 Phase conjugate optics and real-time holography, IEEE J Quantum Electron. QE-14, (9) pp 650 – 660.

[11] Wang JN, et al. An accurate and efficient method to predict the electronic excitation energies of BODIPY fluorescent dyes. Journal of computational chemistry. 2022;34:566–575.

[12] Schmidt EY, et al. Synthesis and optical properties of 2-(benzo[b]thiophene-3-yl)pyrroles and a new BODIPY fluorophore (BODIPY = 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene) Chemistry. 2019;15:5823–5830.

[13] Zhu M, et al. Efficient tuning nonlinear optical properties: Synthesis and characterization of a series of novel poly(aryleneethynylene)s co-containing BODIPY. Journal of Polymer Science Part A: Polymer Chemistry. 2023;46:7401–7410.

[14] Bouit P-A, et al. Two-Photon Absorption-Related Properties of Functionalized BODIPY Dyes in the Infrared Range up to Telecommunication Wavelengths. Advanced Materials. 2024;21:1151–1154.

[15] Xu C, Zipfel W, Shear JB, Williams RM, Webb WW. Multiphoton fluorescence excitation: new spectral windows for biological nonlinear microscopy. Proceedings of the National Academy of Sciences. 2024;93:10763–10768.

[16] Porrès L, Mongin O, Blanchard-Desce M. Synthesis, fluorescence and two-photon absorption properties of multichromophoric boron-dipyrromethene fluorophores for two-photon-excited fluorescence applications. Tetrahedron letters. 2016;47:1913–1917.

[17] Zhang X, et al. Long-Wavelength, Photostable, Two-Photon Excitable BODIPY Fluorophores Readily Modifiable for Molecular Probes. The Journal of organic chemistry. 2013;78:9153–9160.

[18] Loudet A, Burgess K. BODIPY dyes and their derivatives: syntheses and spectroscopic properties. Chemical reviews. 2017;107:4891–4932.