

Research Article

Reverse Saturable Absorption in Substituted Hydrazones and Its Structure-Property Relationship for Photonic Applications

Vijayakumar Sadasivan Nair,¹ Sharafudeen Kaniyarakkal ,²
Shiju Edappadikkunnummal,³ Joicy John,² Sudheesh Palengara,⁴
Siji Narendran,⁵ and Suresh Thelakkadan Puthiyaveetil⁶

¹PG and Research Department of Physics, N S S College Pandalam, Pathanamthitta 689501, Kerala, India

²Department of Physics, Kuwait College of Science and Technology, Doha 35004, Al-Asimah, Kuwait

³International School of Photonics, Cochin University of Science and Technology, Kochi 682022, Kerala, India

⁴Department of Physics, N S S College Manjeri, Malappuram 676122, Kerala, India

⁵Department of Physics, T K M M College Nangiarkulangara, Alappuzha 690513, Kerala, India

⁶Department of Physics, Government Brennen College, Thalassery, Kannur 670106, Kerala, India

Correspondence should be addressed to Sharafudeen Kaniyarakkal; s.valappil@kcst.edu.kw

Received 23 October 2021; Revised 30 March 2022; Accepted 13 April 2022; Published 13 May 2022

Academic Editor: Vincenzo Palleschi

Copyright © 2022 Vijayakumar Sadasivan Nair et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The third-order nonlinear optical properties of three hydrazone derivatives, namely, ethyl 2-((2E)-2-(4-(dimethylamino)benzylidene)hydrazinyl)-5-nitrobenzoate, ethyl 2-((2E)-2-(4-chlorobenzylidene)hydrazino)-5-nitrobenzoate, and methyl 5-nitro-2-((2E)-2-(4-nitrobenzylidene)hydrazino)benzoate were investigated by the single beam Z-scan technique with nanosecond laser pulses at 532 nm. The compounds were doped into PMMA (poly (methyl methacrylate)), and their third-order nonlinearity was studied with a prospective of reaching a compromise between processability and high nonlinear optical behavior. The optical limiting study of the samples was carried out at 532 nm. The measured values of the third-order nonlinear susceptibility, $\chi^{(3)}$, and the nonlinear refractive index, n_2 , are of the order of 10^{-13} esu and 10^{-11} esu, respectively. The nonlinear absorption in materials was attributed to reverse saturable absorption. The results are quite promising for possible applications in photonic devices.

1. Introduction

The prospect of using organics as nonlinear optical materials for photonic switching and optical limiting applications has been the subject of many investigators during the past decade and has a great impact on information technology and industrial applications. In particular, the photonic applications such as all-optical switching, three-dimensional optical devices, all-optical limiting, medical science, and other optical fields [1, 2]. Organic materials are most attractive owing to the known rich variety of organic compounds and the inherent flexibility in synthesizing such compounds with desired properties. The nonlinearity in these molecules has been found to originate from a strong delocalization of π -electrons along the length of the

molecule [3, 4]. By molecular engineering, we can design organic systems for better nonlinear properties, and the study of the linear and nonlinear optical (NLO) coefficients helps us to identify such materials.

The third-order nonlinearity of conjugated organic compounds can be enhanced by (i) increasing the conjugation length, to increase the distance over which charge can be transferred; (ii) creating a donor-acceptor-donor motif by substitution, to increase the extent of charge transfer from the ends of the molecule to the center; and (iii) reversing the sense of symmetric charge transfer by substituting electron acceptors and donors, thereby creating acceptor-donor-acceptor compounds. The above strategy was used in the synthesis of the hydrazone derivatives, which are studied in this report, with a goal to

enhance their nonlinear optical response by modifying the basic structure by substituting various electron donating and electron withdrawing groups [5].

Hydrazone is an efficient class of organic materials for nonlinear optics. Since the hydrazone backbone is an asymmetric transmitter, it strongly increases the molecular nonlinearity for the electron donating and withdrawing group substitutions [6–8]. In this paper, we selected three hydrazone derivatives, namely, ethyl 2-((2*E*)-2-(4-(dimethylamino)benzylidene)hydrazinyl)-5-nitrobenzoate (H1), ethyl 2-((2*E*)-2-(4-chlorobenzylidene)hydrazino)-5-nitrobenzoate (H2), and methyl 5-nitro-2-((2*E*)-2-(4-nitrobenzylidene)hydrazino)benzoate (H3). Sample H1 is substituted with N-N-dimethyl amino group $N(CH_3)_2$, whereas samples H2 and H3 are substituted with Cl and NO_2 groups, respectively. The $N(CH_3)_2$ and Cl groups are electron donors, whereas the NO_2 group is an electron acceptor. Towards identifying efficient nonlinear optical materials, experimental methods such as Z-scan, pump probe, four wave mixing experiments are frequently used [9, 10]. The single beam Z-scan technique is employed to investigate the third-order nonlinear optical properties in these materials. The compounds exhibit noticeable third-order nonlinearity and good optical limiting with nanosecond laser pulses. However, they cannot be directly used in practical devices because they are not flexible like polymers and are degraded when exposed to intense laser beams. To overcome this problem and make use of these materials in devices, the compounds were doped into the PMMA matrix. PMMA is a hard, rigid, and transparent nonlinear optical polymer with a glass transition temperature of 125°C. Its average molecular weight is 60,000. The physical durability of PMMA is far superior than that of other thermoplastics and is tougher than polystyrene. PMMA is most preferred for designing components because of its better resistance to hydrolysis, excellent environmental stability, easy handling and processing, and low cost [11]. This can enhance the opto-chemical and opto-physical stability, as well as the mechanical and thermal properties, while retaining the NLO properties and linear optical transparency [12].

In this article, the Z-scan technique is utilized to study the third-order NLO properties, and structure-property relationship of the hydrazone-based pure compounds in PMMA host using nanosecond laser pulses at 532 nm is reported. The optical limiting studies were also carried out. The relationship between molecular structure and the observed NLO behavior is investigated. In comparison with previously reported works on nonlinear optical coefficient of the PMMA/HQPQ-guest/host system and poly(((s)-1-(4-nitrophenyl)-2-pyrrolidinethyl)methacrylate) (PPM) in PMMA, the third-order nonlinear optical coefficient observed in the present work is one order higher in magnitude [13, 14]. The experimental results reveal that these compounds could be tailored suitably for third-order NLO applications.

2. Experiment

The compounds were synthesized by using the standard procedure [11]. Ethyl-2-hydrazino-5-nitrobenzoate (1.2 g,

0.005 mol) and appropriate aldehyde (0.005 mol) were dissolved in 25 ml of ethanol. To the cold solution, 3 drops of concentrated sulfuric acid was added. Then, the contents were refluxed on a water bath for 8 hrs. Excess ethanol was removed from the reaction mixture under reduced pressure. The solid product obtained was filtered, washed with water, dried, and recrystallized from ethanol—DMF mixture. The structure of the compounds is shown in Figure 1(a).

For doping, both the compound and PMMA were dissolved in dimethyl formamide (DMF) solution. The concentration of the dopant in the PMMA matrix was varied from 5 to 25%. Figure 1(b) shows the linear absorption spectra of the pure compounds recorded at room temperature in DMF solutions using a spectrophotometer (UV-2450 PC Series) and verified that the 532 nm laser excitation falls under nonresonant excitation regime. The linear refractive indices of the samples were measured using a Refracto 30GS digital refractometer. The measurements were performed with 1×10^{-3} mol/L concentration.

3. Z-Scan Measurements

The Z-scan technique is a simple but accurate method to determine both nonlinear index of refraction, n_2 , and nonlinear absorption coefficient, β . Nonlinear index of refraction is proportional to the real part of third-order susceptibility $\text{Re}[\chi^{(3)}]$, and the nonlinear absorption coefficient is proportional to the imaginary part, $\text{Im}[\chi^{(3)}]$ [15]. The schematic of the Z-scan experimental setup is shown in Figure 1(c). By monitoring the transmittance through a small circular aperture placed at the far field position (closed aperture), one can determine the nonlinear refractive index. The nonlinear absorption coefficient of the sample can be determined using the open aperture (OA) Z-scan arrangement [16, 17].

A Q-switched Nd:YAG laser with a pulse width of 7 ns at 532 nm was employed in the experiment. A lens of focal length 23.5 cm was used to focus the laser pulses into a 1mm-quartz cuvette containing sample solution. The closed aperture (CA) Z-scan was performed with 50% aperture. In an attempt to suppress cumulative thermal effects, data were collected in the single shot mode [18]. Furthermore, to determine the effect of the solvent and PMMA to the observed NLO properties, we conducted the Z-scan experiment on the pure DMF and PMMA dissolved in DMF. It does not show any nonlinear effects.

4. Results and Discussion

The nonlinear transmission of the compounds with and without aperture was measured in the far field as the sample is moved through the focal point. The scan was performed at a laser pulse energy of 20 μJ , which corresponds to a peak intensity of 0.735 GW/cm^2 . Assuming a spatial and temporal Gaussian profile for laser pulses, the open aperture (OA) normalized energy transmittance is given by [17, 19]

$$T(z) = \sum_{m=0}^{\infty} \frac{[-q(z)]^m}{(m+1)^{3/2}} \text{ with } q(z) = \frac{\beta_{\text{eff}} I_0 L_{\text{eff}}}{1 + z^2/z_0^2} \quad (1)$$

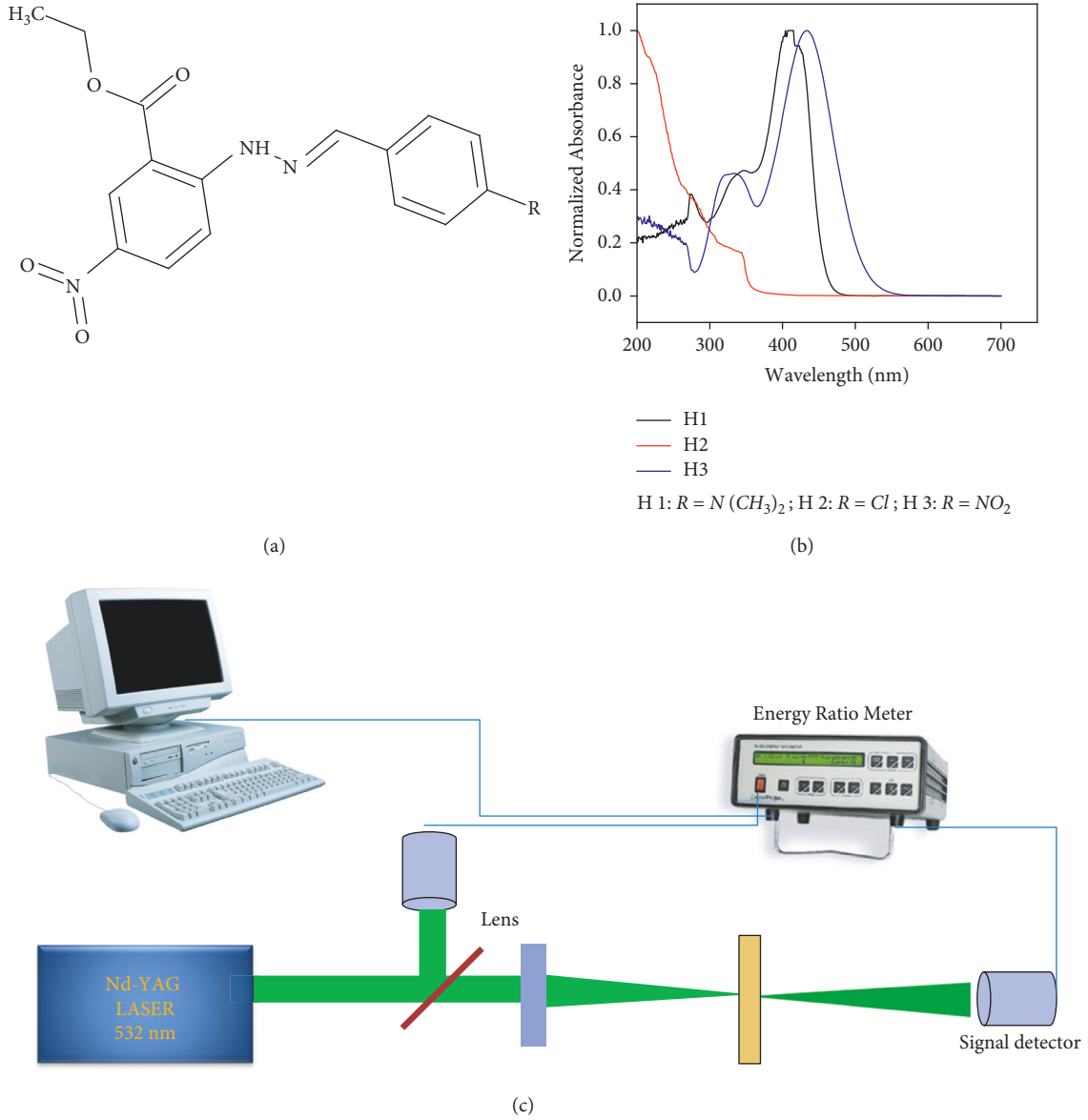


FIGURE 1: (a) Structure of the hydrazone compounds, (b) normalized absorption spectra of the studied compounds, and (c) schematic of the Z-scan experimental setup.

where β_{eff} is the effective two photon absorption coefficient, I_0 is the input irradiance, z is the sample position, $z_0 = \pi\omega_0^2/\lambda$ is the Rayleigh range, ω_0 is the beam waist radius at the focal point ($z = 0$), and λ is the laser wavelength. For fitting the data with equation (1), we consider L_{eff} as the effective path lengths in the case of 2PA and is defined by $L_{\text{eff}} = 1 - e^{-\alpha_0 L}/\alpha_0$, where L is the sample length and α_0 is the linear absorption coefficient. Similarly, for a pure nonlinear refraction curve, obtained by the division method, the normalized transmittance is given by [20–22]

$$T = 1 - \frac{4\Delta\phi_0 x}{(x^2 + 1)(x^2 + 9)}, \quad (2)$$

where $\Delta\phi_0$ is the on-axis nonlinear phase shift at the focus and $x = z/z_0$. The nonlinear refractive index γ (m^2/W) can

be determined from the equation $\Delta\phi_0 = k\gamma I_0 L_{\text{eff}}$, where $k = 2\pi/\lambda$ is the wave vector and λ is the wavelength.

$$I_0 = \frac{4\sqrt{\ln 2} E_{\text{total}}}{\sqrt[3]{\pi}\omega_0^2 \tau}, \quad (3)$$

where E_{total} is the incident energy on the sample after reflection from the front surface of the cuvette is taken into account and τ is the pulse width of the laser. The nonlinear refractive index n_2 (esu) can be calculated from the conversion formulae:

$$n_2 \text{ (esu)} = \left(\frac{cn_0}{40\pi}\right)\gamma \left(\frac{\text{m}^2}{\text{W}}\right), \quad (4)$$

where n_0 the linear refractive index and c is the velocity of light in vacuum.

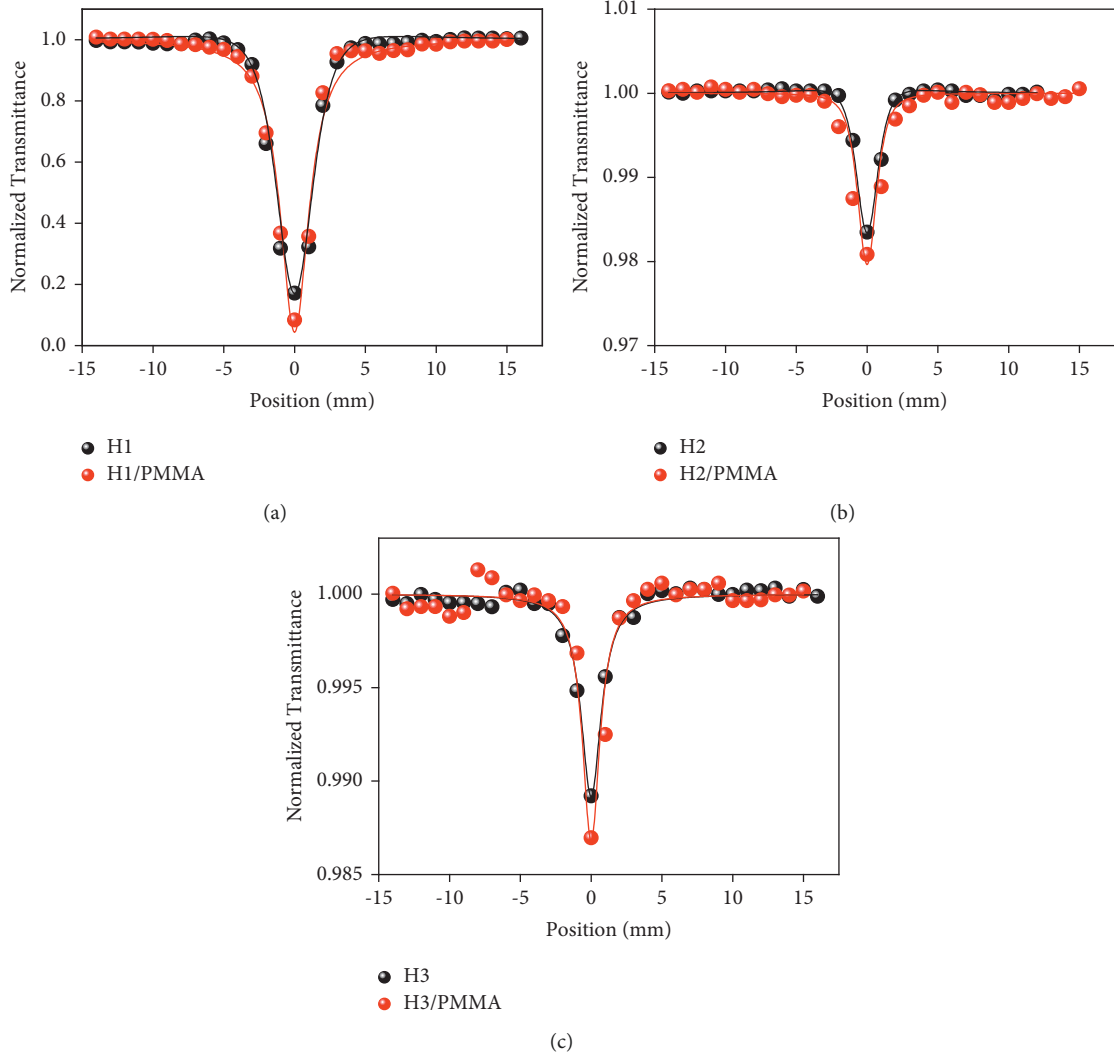


FIGURE 2: Open aperture Z-scan curves for pure and PMMA-doped compounds. The open circles represent experimental data, while the solid line represents theoretical fit with $\beta_{\text{eff}} = 2 \text{ cm/GW}$, 0.0364 cm/GW , and 0.0258 cm/GW for H1, H2, and H3, respectively, and $\beta_{\text{eff}} = 2.2 \text{ cm/GW}$, 0.047 cm/GW , and 0.032 cm/GW for H1/PMMA, H2/PMMA, and H3/PMMA, respectively.

The normalized OA curve for the pure compounds and the compounds with PMMA (concentration of 25% in matrix) dissolved in DMF is shown in Figure 2. The solid lines are the theoretical fit of equation (1) to the experimental data, which yields the value of effective two photon absorption coefficient β_{eff} .

The pure nonlinear refraction curve obtained for pure compounds H1 and H1/PMMA is shown in Figure 3. Here, the solid lines are theoretical fit of the experimental data to equation (2).

The real and imaginary part of the third-order nonlinear optical susceptibility $\chi^{(3)}$ can be calculated according to the following relations:

$$\begin{aligned} \text{Re}\chi^{(3)} &= 2n_0^2\varepsilon_0c\gamma, \\ \text{Im}\chi^{(3)} &= \frac{n_0^2\varepsilon_0c\beta\lambda}{2\pi}, \end{aligned} \quad (5)$$

where n_0 is the linear refractive index, ε_0 is the vacuum permittivity, and c is the velocity of light in vacuum.

Second-order hyperpolarizability γ_h which describes the nonlinear induced polarization per molecule, in an isotropic medium, is related to the third-order bulk susceptibility as [23–25]

$$\gamma_h = \frac{\chi^{(3)}}{[(1/3)(n_0^2 + 2)]^4 N}, \quad (6)$$

where N is the density of molecules in the unit of molecules per cm^3 , n_0 is the linear refractive index of the medium, and $\chi^{(3)} = \sqrt{(\text{Re}\chi^{(3)})^2 + (\text{Im}\chi^{(3)})^2}$.

The values of γ_h for the pure compounds and the compounds in PMMA is of the order of 10^{-31} esu, which is well comparable with the value reported for silicon naphthalocyanine, SiNc ($\gamma_h = 1.7 \times 10^{-31}$ esu), a widely known optical limiting material [26]. The calculated values of n_2 ,

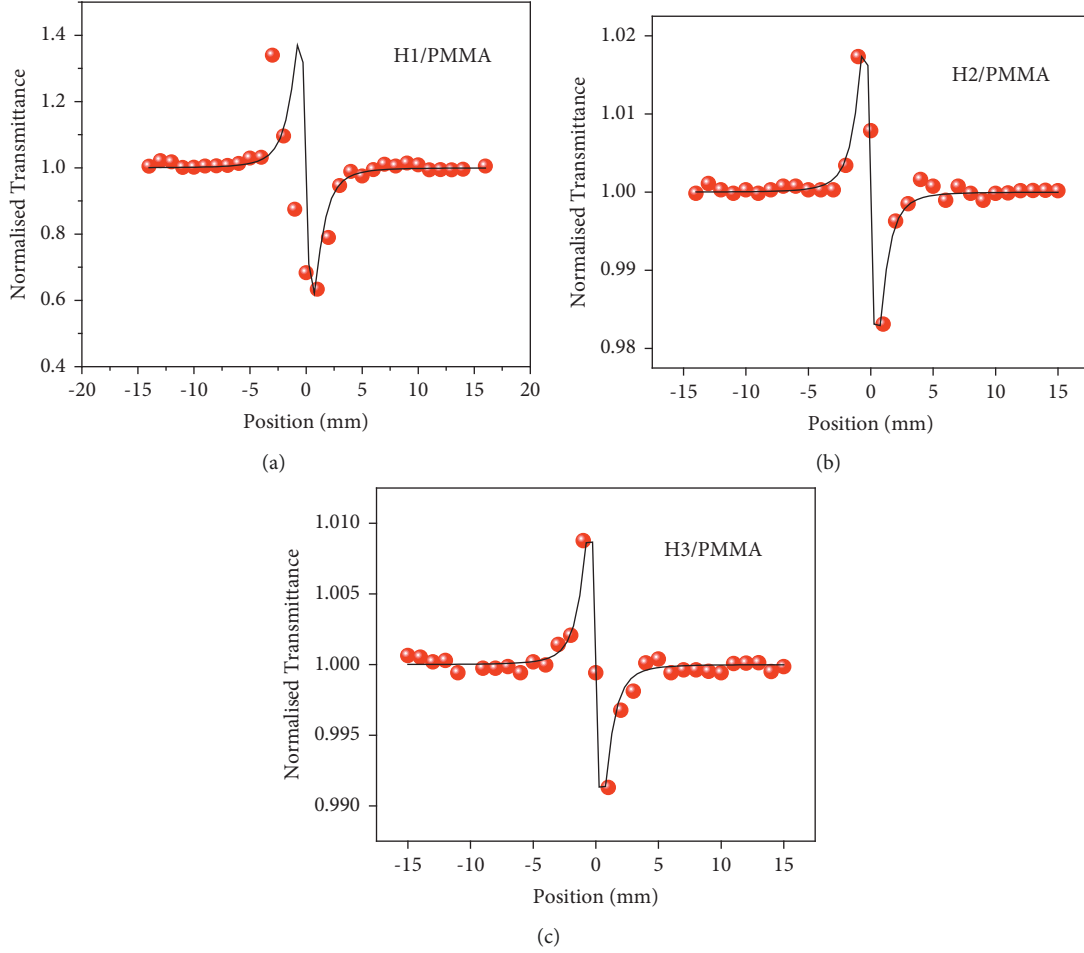


FIGURE 3: Pure nonlinear curves obtained by the division method for pure compounds doped with PMMA. Solid lines are theoretical fit of the experimental data to equation (2).

TABLE 1: Values of $\text{Re}\chi^{(3)}$, $\text{Im}\chi^{(3)}$, n_2 , and γ_h determined experimentally for pure compounds.

Sample	$\text{Re}\chi^{(3)}$ ($\times 10^{-13}$ esu)	$\text{Im}\chi^{(3)}$ ($\times 10^{-13}$ esu)	n_2 ($\times 10^{-11}$ esu)	γ_h $\times 10^{-31}$ (esu)
H1	-9.060	0.312	-8.380	4.570
H2	-0.957	0.005	-0.888	0.537
H3	-0.488	0.004	-0.453	0.326

TABLE 2: Values of $\text{Re}\chi^{(3)}$, $\text{Im}\chi^{(3)}$, n_2 , and γ_h determined experimentally for the compounds doped with PMMA.

Sample	$\text{Re}\chi^{(3)}$ ($\times 10^{-13}$ esu)	$\text{Im}\chi^{(3)}$ ($\times 10^{-13}$ esu)	n_2 ($\times 10^{-11}$ esu)	γ_h $\times 10^{-31}$ (esu)
H1	-10.47	0.343	-9.640	5.290
H2	-1.060	0.007	-0.981	0.537
H3	-0.641	0.004	-0.595	0.326

$\text{Re}\chi^{(3)}$, $\text{Im}\chi^{(3)}$, and γ_h for the pure compounds and compounds doped with PMMA are shown in Tables 1 and 2.

The dependence of the nonlinear absorption (NLA) coefficient with on-axis irradiance gives the information about the mechanism of the nonlinear absorption. Generally, nonlinear absorption can be caused by free carrier absorption, saturable absorption, and direct multiphoton

absorption or excited state absorption. From our observations, it is seen that β_{eff} is decreasing with increasing intensity for all the compounds and intercept on the vertical axis is nonzero, as shown in Figure 4. The fall of β_{eff} with increasing I_0 is a consequence of reverse saturable absorption (RSA) [27, 28]. RSA generally arises in a molecular system where the presence of excited-state absorption to a

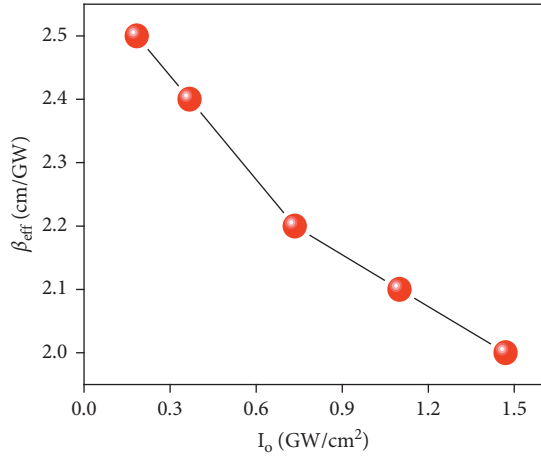


FIGURE 4: Variation of β_{eff} with on-axis intensity I_0 within the compound H1.

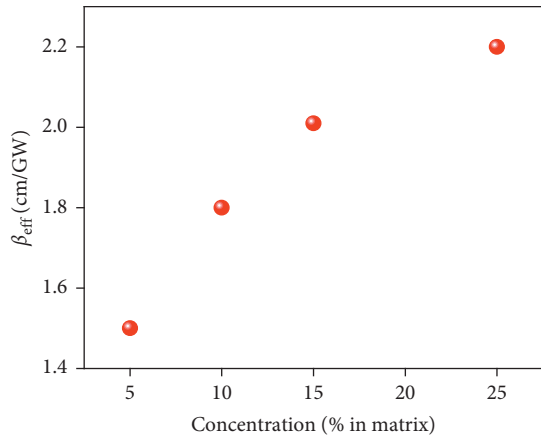


FIGURE 5: β_{eff} vs. concentration of the sample H1 in the polymer matrix.

higher lying state occurs. In particular, when the excited state absorption cross section is larger than the ground state cross section [29]. To confirm the presence of RSA, we calculated the absorption cross-sections in the ground and excited states. The excited state cross section σ_{ex} can be calculated from the normalized Z-scan data as the procedure described in the literature [30, 31].

The ground state absorption cross section σ_g can be calculated from the following equation:

$$\alpha = \sigma_g N_a C, \quad (7)$$

where N_a is the Avogadro number, C is the concentration in moles/cm³, and α is the linear absorption coefficient.

The calculated values of σ_{ex} for the pure compounds H1, H2, and H3 are 1.522×10^{-17} cm², 1.475×10^{-18} cm², and 1.43×10^{-18} cm², respectively. For compounds H1, H2, and H3 doped with PMMA, the values of σ_{ex} are 1.739×10^{-17} cm², 1.656×10^{-18} cm², and 1.50×10^{-18} cm², respectively. The values of σ_g for the compounds H1, H2, and H3 are calculated as 2.075×10^{-18} cm², 8.30×10^{-21} cm², and 1.66×10^{-21} cm², respectively. It is seen that the value of

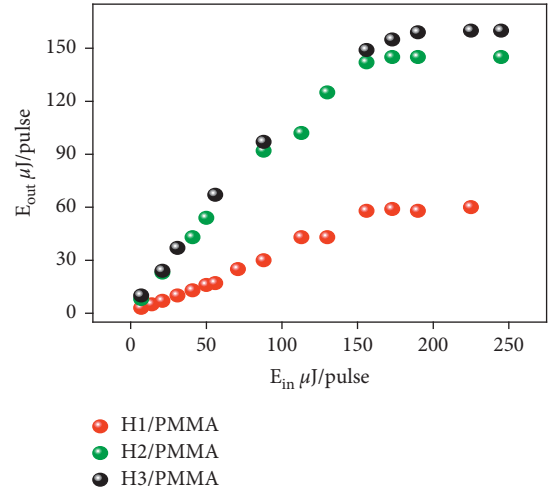


FIGURE 6: Optical limiting behavior in the compounds doped with PMMA.

σ_{ex} is larger than the value of σ_g for both pure compounds and compounds doped with PMMA which is in agreement with the condition for reverse saturation absorption (RSA) [32].

The dependence of β_{eff} on the concentration of the sample in the polymer matrix is shown in Figure 5.

Based on the strong reverse saturated absorption, a good optical limiting of nanosecond laser pulses of the samples can be expected. Figure 6 shows the optical limiting behaviour of the compound doped with PMMA. It can be seen that the best limiting behaviour is observed with sample H1, which exhibits strongest nonlinear absorption among the samples. For incident energies less than 100 μ J/pulse, the output linearly increases with the input. But for energies more than 100 μ J/pulse, optical limiting of the pulses was observed. For input energies well below 250 μ J, there is no damage observed in the samples. But beyond 300 μ J, there is a deviation from the optical limiting behaviour. It could be due to damage of sample with laser pulses.

These results show that the compounds exhibit larger third-order NLO properties in PMMA host as compared to the pure compounds. The π -electrons associated with the dopant molecules will form an electron cloud around the chain and can be distorted by applying an electric field, which results in variation of nonlinear effects in the samples. Even though the enhancement of NLO properties is very low, PMMA is most preferred because of its flexibility and good resistance having a low density that aids fabrication of lightweight components, and it increases the damage threshold of the compounds.

From the results, we noticed that the nonlinear response among the three hydrazone derivatives is of the order H1 > H2 > H3. In the case of H1, the highly electron donating dimethyl amino group—N(CH₃)₂—is attached to the para position. Thus, compared to the acceptor group on the left-hand side, in which the carbon ring is attached to the highly electron accepting NO₂ at the metaposition and ester group at the ipso position, the right-hand side of the molecule acts as a donor giving away electrons easily to form

a stable π -electron distributed system. Hence, there is a strong delocalization of electrons in the molecule that gives rise to the large nonlinear polarization. Consequently, the highest nonlinear response was observed with H1. In case of H2, chlorine atom is attached at the para position. Cl is an amphiprotic group, and its contribution to the molecular hyperpolarizability depends on the strength of the acceptor group attached to the phenyl ring of the molecule [33]. Since the acceptor group at the left-hand side is very strong, the Cl atoms acts as a donor. But in H3, a strong acceptor NO₂ group is attached at the para position. The NO₂ groups at both ends accept electrons, and hence, delocalization decreases in the molecule.

It can be noted that enhancement of PMMA nonlinear optical properties by means of a quinoid molecule was reported with $\chi^{(3)}$ values of 10^{-14} esu [13]. It is also noted that $\chi^{(3)}$ value of ethyl 2-((2E)-2-(4-(dimethylamino)benzylidene)hydrazinyl)-5-nitrobenzoate is comparable with the values of the order of 10^{-13} esu of many varieties of azo dyes, which are well-known third-order nonlinear optical materials [34]. Thus, the work reported here reveals that these compounds are one of the suitable classes of nonlinear optical material for photonic applications.

5. Conclusions

The third-order nonlinear properties of hydrazone derivatives with different substituents were investigated using the single-beam Z-scan technique with 7 ns laser pulses at 532 nm. For making effective use of this materials in devices, the compounds were doped into poly(methylmethacrylate), and the third-order optical properties were studied. The results show that the compounds exhibit larger third-order NLO properties in PMMA host as compared to the pure compounds. The calculated values of nonlinear refractive index and second-order hyperpolarizability are of the order of 10^{-11} esu and 10^{-31} esu, respectively. Hence, these hydrazones can be suitable materials for photonic applications.

Data Availability

Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare no conflicts of interest.

Acknowledgments

S. K acknowledges Kuwait Foundation for the Advancement of Sciences (KFAS), Kuwait, for the research grant (no:PR18-13SP-01). E. Shiju acknowledges SERB, India, for providing financial assistance through NPDF (PDF/2020/002494). This research was funded by the Kuwait Foundation for the

Advancement of Sciences (KFAS), Kuwait (grant no.PR18-13SP-01).

References

- [1] J. Zyss, *Molecular Nonlinear Optics Materials. Physics and Devices*, Academic Press Inc, London, UK, 1994.
- [2] R. W. Munn and C. N. Ironside, Eds., *Principles and Applications of Nonlinear Optical Materials*, Chapman and Hall: CRC Press, Boca Raton, FL, USA, 1993.
- [3] S. Raghavendra, T. Chandra Shekhara Shetty, C. S. Chidan Kumar et al., "Novel acentric D- π -A- π -D nonlinear optical (2E, 4E)-[dimethylamino phenyl]-1-(4methylphenyl)penta-2,4-dien-1-one crystal for second and third order nonlinear applications," *Journal of Chemical Sciences*, vol. 132, no. 1, p. 70, 2020.
- [4] Q. Feng, Y. Li, G. Shi et al., "A photo-controllable third-order nonlinear optical (NLO) switch based on a rhodamine B salicylaldehyde hydrazone metal complex," *Journal of Materials Chemistry C*, vol. 4, no. 36, pp. 8552–8558, 2016.
- [5] M. Albota, D. Beljonne, J.-L. Bredas et al., "Design of organic molecules with large two-photon absorption cross sections," *Science*, vol. 281, no. 5383, pp. 1653–1656, 1998.
- [6] F. Pan, M. S. Wong, M. Bosch, C. Bosshard, U. Meier, and P. Gunter, "A highly efficient organic second-order nonlinear optical crystal based on a donor-acceptor substituted 4-nitrophenylhydrazone," *Applied Physics Letters*, vol. 71, no. 15, pp. 2064–2066, 1997.
- [7] C. Zhang, X. Li, Y. Wang, M. An, and Z. Sun, "A hydrazone organic optical modulator with a π electronic system for ultrafast photonics," *Journal of Materials Chemistry C*, vol. 9, no. 34, pp. 11306–11313, 2021.
- [8] W. Xu, Z. Shao, Y. Han, W. Wang, Y. Song, and H. Hou, "Light-adjustable third-order nonlinear absorption properties based on a series of hydrazone compounds," *Dyes and Pigments*, vol. 152, pp. 171–179, 2018.
- [9] S. Anandan, S. Manoharan, N. K. Siji Narendran, and T. C. Sabari Girisunb, "Donor-acceptor substituted thiophene dyes for enhanced nonlinear optical limiting," *Optical Materials*, vol. 85, pp. 18–25, 2018.
- [10] A. U. Habeeba, M. Saravanan, T. S. Girisun, and S. Anandan, "Nonlinear optical studies of conjugated organic dyes for optical limiting applications," *Journal of Molecular Structure*, vol. 1240, Article ID 1240130559, 2021.
- [11] B. S. Furniss, A. J. Hannaford, P. W. G. Smith, and A. R. Tatchell, *Vogel's Textbook of Practical Organic Chemistry*, Pearson Education, Singapore, 5th edition, 2005.
- [12] F. W. Billmeyer Jr., *Text Book of Polymer Science*, John Wiley & Sons, Singapore, 3rd edition, 1994.
- [13] F. D'Amore, M. Lanata, S. M. Pietralunga, M. C. Gallazzi, and G. Zerbi, "Enhancement of PMMA nonlinear optical properties by means of a quinoid molecule," *Optical Materials*, vol. 24, no. 4, pp. 661–665, 2004.
- [14] H. L. Saadon, "Z-scan studies and optical limiting in a new organic-polymer composite film," *Optical and Quantum Electronics*, vol. 48, no. 1, p. 40, 2016.
- [15] J. L. Bredas, C. Adant, P. Tackx, A. Persoons, and B. M. Pierce, "Third-order nonlinear optical response in organic materials: theoretical and experimental aspects," *Chemistry Review*, vol. 94, no. 1, pp. 243–278, 1994.
- [16] M. Sheik-Bahae, A. A. Said, and E. W. VanStryland, "High-sensitivity, single-beam n₂ measurements," *Optics Letters*, vol. 14, no. 17, pp. 955–957, 1989.

- [17] M. Sheik-Bahae, A. A. Said, T.-H. Wei, D. J. Hagan, and E. W. VanStryland, "Sensitive measurement of optical nonlinearities using a single beam," *IEEE Journal of Quantum Electronics*, vol. 26, no. 4, pp. 760–769, 1990.
- [18] P. Yang, J. Xu, J. Ballato, R. W. Schwartz, and D. L. Carroll, "Optical limiting in $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and $\text{PbZrTi}_{1-x}\text{O}_3$ ferroelectric thin films," *Applied Physics Letters*, vol. 80, no. 18, pp. 3394–3396, 2002.
- [19] R. L. Sutherland, *Handbook of Nonlinear Optics*, Dekker, New York, NY, USA, 1996.
- [20] G. Muruganandi, M. Saravanan, G. Vinitha, M. B. Jessie Raj, and T. C. Sabari Girisun, "Effect of reducing agents in tuning the third-order optical nonlinearity and optical limiting behavior of reduced graphene oxide," *Chemical Physics*, vol. 488–489, pp. 55–61, 2017.
- [21] G. Muruganandi, G. Saravanan, M. B. Vinitha, T. C. Jessie Raj, and S. GirisunBarium, "Barium borate nanorod decorated reduced graphene oxide for optical power limiting applications," *Optical Materials*, vol. 75, pp. 612–618, 2018.
- [22] T. C. Sabari Girisun, M. Saravanan, and V. R. Soma, "Wavelength-dependent nonlinear optical absorption and broadband optical limiting in $\text{Au-Fe}_2\text{O}_3\text{-rGO}$ nanocomposites," *ACS Applied Nano Materials*, vol. 1, no. 11, pp. 6337–6348, 2018.
- [23] M.-T. Zhao, B. P. Singh, and P. N. Prasad, "A systematic study of polarizability and microscopic third-order optical nonlinearity in thiophene oligomers," *The Journal of Chemical Physics*, vol. 89, no. 9, pp. 5535–5541, 1988.
- [24] R. Shivaraj, P. S. Patil, P. Maidur, and S. Patil, "Linear optical and third-order nonlinear optical properties of anthracene chalcone derivatives doped PMMA thin films," *Optik*, vol. 190, pp. 54–67, 2019.
- [25] R. Shivaraj, M. Parutagouda, S. Patila et al., "Molecular structure, second- and third-order nonlinear optical properties and DFT studies of a novel non-centrosymmetric chalcone derivative: (2E)-3-(4-fluorophenyl)-1-(4-[(1E)-(4-fluorophenyl)methylene]amino}phenyl)prop-2-en-1-one," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 184, pp. 342–354, 2017.
- [26] F. Guo, W. Sun, D. Wang, L. Zhao, Z. Lu, and Y. Nie, "Optical limiting of pentaazadentate metal complexes for picosecond pulses in solution," *Applied Optics*, vol. 40, no. 9, p. 1386, 2001.
- [27] S.-L. Guo, L. Xu, H. T. Wang, X. Z. You, and N. B. Ming, "Investigation of optical nonlinearities in $\text{Pd}(\text{po})_2$ by Z-scan technique," *Optik*, vol. 114, no. 2, pp. 58–62, 2003.
- [28] S. Couris, E. Koudoumas, A. A. Ruth, and S. Leach, "Concentration and wavelength dependence of the effective third-order susceptibility and optical limiting of C_{60} in toluene solution," *Journal of Physics B: Atomic, Molecular and Optical Physics*, vol. 28, no. 20, pp. 4537–4554, 1995.
- [29] C. Torres-Torres, A. V. Khomeenko, L. Tamayo-Rivera, R. Rangel-Rojo, Y. Mao, and W. H. Watson, "Measurements of nonlinear optical refraction and absorption in an amination triazole push-pull derivative by a vectorial self-diffraction method," *Optics Communications*, vol. 281, no. 12, pp. 3369–3374, 2008.
- [30] F. Z. Henari, W. J. Blau, L. R. Milgrom, G. Yahioglu, D. Phillips, and J. A. Lacey, "Third-order optical non-linearity in Zn (II) complexes of 5, 10, 15, 20-tetraarylethynyl-substituted porphyrins," *Chemical Physics Letters*, vol. 267, no. 3–4, pp. 229–233, 1997.
- [31] E. Garoni, A. Colombo, K. Kamada, C. Dragonetti, and D. Roberto, "Impact of the subunit arrangement on the nonlinear absorption properties of organometallic complexes with ruthenium(II) σ -acetylide and benzothiadiazole as building units," *Inorga*, vol. 7, no. 5, p. 67, 2019.
- [32] L. W. Tutt and T. F. Boggess, "A review of optical limiting mechanisms and devices using organics, fullerenes, semiconductors and other materials," *Progress in Quantum Electronics*, vol. 17, no. 4, pp. 299–338, 1993.
- [33] L. H. Honark, *Polymers for Light Wave and Integrated Optics*, MarcelDekker, New York, NY, USA, 1992.
- [34] C. W. Ghanavatkar, V. R. Mishra, and N. Sekar, "Review of NLOphoric azo dyes—developments in hyperpolarizabilities in last two decades," *Dyes and Pigments*, vol. 191, Article ID 109367, 2021.