Chapter 4
Investigation of Indole-based molecular systems for nonlinear optical applications

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CHAPTER 4
INVESTIGATION OF INDOLE BASED MOLECULAR SYSTEMS FOR NONLINEAR OPTICAL APPLICATIONS

This chapter describes the results of Z-scan and optical limiting experiments on a series of indole based polymeric molecular systems. We could observe phenomenal growth in the nonlinear optical parameters of the polymeric versions compared to its monomeric unit i.e. indole (IND-1). Indole hardly showed any nonlinear optical properties under nanosecond excitation regime; on the other hand, its polymeric counterparts like polyindole (IND-2), Allyl polyindole (IND-3), Benzyl polyindole (IND-4) etc displayed all essential properties of fairly good nonlinear optical materials. Optical limiting and degenerate four wave mixing studies were also conducted on these molecules. Molecules showed excellent optical limiting property with low limiting threshold. Possible mechanisms responsible for the nonlinear absorption property of each molecule have been discussed. To investigate the nonlinear response of the samples in solid state form, some of the samples were studied in its thin film form by doping in PMMA matrix. Lorentzian-Gaussian fitted PL spectra were also studied to understand its emission properties.

4.1 INTRODUCTION

Indole, a white solid at room temperature, is an aromatic heterocyclic molecule consisting of a six-membered benzene ring, fused with five-membered nitrogen-containing pyrrole ring. Historically, the name indole has been evolved from two words ‘indigo’ and ‘oleum’, since indole was first synthesized by the treatment of the indigo dye with oleum. It is an abundantly found compound in mother-nature and is produced by a variety of bacteria in its routine physiological process. 2.5% of natural jasmine oil contains pure indole. It was first synthesized by Adolf von Baeyer [1] in 1866 by reducing oxyindole with zinc dust. In the mid 1930’s it was identified that the key component of many alkaloids and auxins is indole. Subsequently, active research has been carried out on the derivatives of indole and its polymerized forms for various chemical, electronic and biological applications.

Polyindole (IND-2) and its various derivatives offer several applications including applications in fields like electronics [2], electro catalysis [3], drug delivery [4], sensor applications [5], anticorrosion coatings [6], battery electrode [7], etc. However, no work has so far been reported employing polyindole as a third order nonlinear optical material with its
potential applications in optical limiting devices. The chemical and electrochemical synthesis of polyindole has been discussed in detail by Billaud and co-workers [8]. Here, chemical oxidative route of Indole has been chosen for the synthesis of IND-2 and other derivatives because it offers mass production at reasonable cost. Basically compound IND-2 is a very good conducting polymer. The key advantages of polymerized indole-based compounds over other type of conducting polymers are the high redox activity, good thermal stability, and slow degradation rate etc [9, 10]. One of the remarkable features of polymerized indole over its monomer counterpart is its observed large value of third order nonlinear optical coefficients [11]. Meanwhile, indole monomer hardly shows any nonlinear optical effects. This chapter also explores the physical origin of nonlinearity in various indole based polymeric systems and its non-occurrence in indole.

4.2 INDOLE BASED MOLECULAR SYSTEMS

In the present work, IND-1 (Indole) is used as the basic building block. Three different polymeric forms were derived out of it via in-situ polymerization technique. In addition to the commonly found polyindole (IND-2) version, we also conducted nonlinear optical studies on the Allyl (IND-3) and Benzyl (IND-4) version of the Indole; these molecules possess highly conjugated molecular structure which could provide them a highly extended $\pi$-electron system [12].

4.3 SYNTHESIS OF THE COMPOUNDS

All reagents such as monomer indole, oxidant ammonium peroxydisulfate, ethanol, potassium carbonate, allyl bromide etc were of analytic grade and were procured from Sigma Aldrich, India. Solvents like acetone, dimethyl sulfoxide, N,N-dimethyl formamide were synthetically pure and further purified by double distillation.

4.3.1. Indole (IND-1)

Analytical grade pure indole was procured from Sigma Aldrich. Anal. Calc for $C_9H_2N_1$, Composition: C (82.02%), H (6.02%), N (11.96%); MW:117.15, UV-vis: $\lambda_{max}$/nm (DMSO)~267, FT-IR:v$_{max}$/cm$^{-1}$ (KBr phase) 3380 (-NH vib.), 1570 (C=C vib.), 1550 (-NH def. vib.), 1505 (C=C vib.), 1352 (C=C stretch. vib.), 1045 (C-C stretch.), 748 (out of plane def.), 735 (out of plane vib.of C$_2$-H), 725 (out of plane vib. of C$_3$-H).
4.3.2. Polyindole (IND-2)

Polyindole (in many literature also known as PIN) is synthesized via in-situ polymerization of indole (IN) monomer (1H-Benzo[b]pyrrole) by chemical oxidation at 20–25 °C, using 0.5 molar ammonium peroxydisulfate as an oxidant (Figure 1). Firstly, 0.5 molar aqueous solution of indole monomer is ultrasonicated for a period of 20 minutes. Ammonium peroxydisulfate is then added drop-wise into the stirred solution at 10°C. The polymerization is carried out at room temperature for 8 hrs with constant magnetic stirring (Tarsons SPINOT digital magnetic stirrer). On adding oxidant to the indole solution, the colour changes from pale green to dark, indicating the onset of polymerization and at the end of the stirring, solution completely turns to dark black. The product thus formed is in the form of a suspension and hence subjected to filtering at 20 °C. The resulting residue is washed several times with distilled water and ethanol to remove any unreacted components present, and then vacuum dried at 50 °C for 4 hrs. The resulting powder obtained is polyindole [18].

UV-vis: $\lambda_{\text{max}}$/nm (DMSO) ~278, 319, FT-IR: $\nu_{\text{max}}$/cm$^{-1}$ (KBr phase) 3409 (N-H stretch.), 3382 (-N-H stretch vib.), 1636 (~C=C vib.), 1597 (N-H deform.), 1540 (N-H stretch.), 1366 (C8-N-C2-C3- stretch.), 1191 (N-H stretch.), 767 (-C$_2$-H vib.), 742 (benzene ring stretch.) [13].

4.3.3. Allyl polyindole (IND-3)

1.1 g of indole, dissolved in 10ml of DMF was stirred for 30 minutes with 3 equivalent of K$_2$CO$_3$ at 50°C. After cooling to room temperature 1.21 gm of allyl bromide is added along with ammonium peroxydisulfate and stirred for 6 hours. The solution is poured into ice-cold water and the precipitate is washed with distilled water. The resulting product is baked in an oven and vacuum dried. UV-vis: $\lambda_{\text{max}}$/nm (DMSO)~264, 295, FT-IR: $\nu_{\text{max}}$/cm$^{-1}$ (KBr phase) 3393.1(-OH stretching), 2924.5 (asymmetric C-H stretching), 2853 (N-H stretching), 1620.8 (ring stretching vib.), 1471.4 (ring vib.), 1385.6 (-C-H deformation vib.), 1338.3 (-C-H deformation vib.), 1240.9 (C=C stretching), 1045.2 (N-H & C-H deformation), 748.2 (-CH def. vib.), 619 (CH$_2$=CH-R twisting vib.) [14].
4.3.4. Benzyl polyindole (IND-4)

1.5 g of indole, dissolved in 15 ml of DMF was stirred for 30 minutes with 3 equivalent of K$_2$CO$_3$ at 50°C. After cooling to room temperature 1.6 gm of benzyl bromide is added and stirred along with ammonium peroxodisulfate for 6 hours. The solution is poured into ice-cold water and the precipitate is washed with distilled water. All other reagents used and procedures are the same as shown in section 4.3.2 and the resulting product obtained is benzyl polyindole. UV-vis: $\lambda_{max}$/nm (DMSO)$\sim$268, FT-IR: $\nu_{max}$/cm$^{-1}$ (KBr phase) 3396.9 (N-H stretching), 2923.5 (-OH stretching), 2852.2 (-CH stretching), 1462.7 (C=C & C=N in plane vib.), 1399.1 (=CH def. vib.), 1349.9 (CH2 def. vib), 1187.9 (-C-H skeletal vib.), 1127.73 (C-N stretching), 750.2 (out of plane def. vib. of benzene), 619 (C=N twisting vib.). FTIR spectra of all the samples are taken in KBr is shown in Figure 4.1.

![Figure 4.1 FTIR spectra of indole compounds taken in KBr disc.](image)

Essentially, it is found that there are two possible types of mechanisms [15] which play role in the polymerization of indole: 1, 3-position or the 2, 3-position. For 1, 3-position, the main conjugate backbone is (-N-CH=CH-)$_n$ whereas for 2,3-position it rather follows (-CH=CH-)$_n$ configuration. FT-IR can provide useful information about the polymerization dynamics. As the polymerized molecules display, the crucial role of bond formation is played
by the five-membered pyroll ring moiety. 1, 2, and 3 positions are equally involved in bond formation. As per reference [15], 1-3, 2-3, 1-1:3-3 and 2-2:3-3 configurations are equally possible. Based on FTIR and NMR results Xu et al [16] have suggested that possible polymerization mechanism can involve only positions 2 and 3 as shown in the case of IND-2. However in a recent report, [17] by doping with CdSe nanoparticles, it has been established that 2-3 positions are the most probable site for polymerization in IND-2; whereas in other derivatives like IND-3, nitrogen site also act as a bonding point where it mobilizes the charge carriers across the polymer backbone. There are various interpretations by different research groups on the probable mechanism involved in the polymerization of indole (IND-1) to form its polymerized versions.

4.4 MOLECULAR STRUCTURES

Two dimensional image of the molecular structure of the compounds are shown in Figure 4.2

![Indole (IND-1)](image1)
![Polyindole (IND-2)](image2)
![Allylpolyindole (IND-3)](image3)
![Benzylpolyindole (IND-4)](image4)

**Figure 4.2** Two dimensional representations of molecular structures of Indole based molecular systems.
4.5. LINEAR ABSORPTION STUDIES

The electronic absorption spectra arise from transitions between electronic energy levels, accompanied by changes in both vibrational and rotational states. Since the wavelength of absorption is a measure of the separation of energy levels of the orbitals concerned, a transition between these levels, when gaseous sample is irradiated, gives rise to fine structure consisting of distinct lines, whereas, in case of solutions, it merge to evolve into a broad absorption band. Hence electronic absorption spectra are usually broad as compared to FT-IR or NMR.

4.5.1. Optical absorption spectra

Linear absorption spectra of IND-1 and its polymeric forms are shown in Figure 4.3. Absorption of UV-Vis wavelengths by the compounds provides information about the electronic transitions occurring in the molecules and their linear absorption properties at low intensity regime. In organic molecules, electronic transitions generally occur between bonding and nonbonding orbitals to unoccupied antibonding orbitals. This electronic excitations result in a sharp increase in the value of the absorption coefficient (α) at the corresponding wavelengths [18, 9].

Figure 4.3 a) UV-Vis. spectra of IND-1 and IND-2 in DMSO.
For IND-1, dissolved in DMSO, the plot shows peak at 273 nm, whereas for IND-2, the peaks are positioned at 278 and 319 nm under similar conditions. IND-2 shows comparatively higher extent of bathochromic shift with respect to the IND-1 peak, a likely symptom of improved electronic conjugation, and this in turn, contributes to the enhanced delocalization of electrons along the π bonds in IND-2. The monomer peak at 273 nm for IND-1 originates due to n→π* transitions which is the outcome of transition between non-bonding atomic orbitals holding unshared pair of electrons and anti-bonding π-orbitals which falls in the R-band. Similar n→π* transition peaks can be observed in IND-2 spectrum with one at 278 nm and another at 319 nm [19]. IND-3 has two absorption peaks, one at 264 and another at 295 nm. Both correspond to n→π* type of transitions. It is notable that linear absorption at 264 nm is likely to induce two-photon based nonlinear absorption under laser excitation. The compound IND-4 has only one absorption peak at 268 nm. In brief, the spectra reveal that all the compounds except IND-1 show finite amount of residual absorption at the excitation wavelength, which could lead to excited state type of absorption (ESA) upon highly intense optical excitation.

4.5.2. Tauc plots of the compounds

In order to understand the optical band gap of the compounds, Tauc plots of the compounds were traced using UV-Vis data and are presented in Figure 4.4. To extract the band gap value, the incident photon energy (in eV) versus linear absorption, in terms of
were plotted and the tangent drawn at the linear regime of the trace gives the band gap value on the abscissa [20].

The estimated band gap values of IND-1, IND-2, IND-3 and IND-4 respectively were in the order of 4.19, 2.52, 3.55, and 3.11 eV [21]. Since IND-2 exhibits the lowest band gap, it is likely to exhibit the strongest nonlinearity under the short pulse (2.33 eV, 7 ns) excitation regime. Further, band gap of IND-1 is the highest among the samples investigated; hence it is likely to show the lowest NLO response.

4.6 Z-SCAN STUDIES

We used 7 nanosecond optical pulses from a Q-switched, frequency doubled Nd:YAG laser, emitting at 532 nm wavelength. Intensity dependent transmittance was measured using the Z-scan set up outlined in Chapter 2.

Figure 4.4 Tauc plots of the indole-based oligomeric systems showing the optical band gap of the compounds recorded in DMSO solvent.
4.6.1 Open Aperture Z-scan studies

The procedure outlined in reference [22] was used to record the open aperture Z-scan signals of the samples dissolved in DMSO at a concentration of 0.05(% m/v). Data were recorded in single shot mode to minimise the cumulative thermal contributions to the nonlinearity. A lens of focal length 15cm was used, which reduced the beam waist radius to an estimated value of 17.56µm at the focal spot and the resulting Rayleigh range ($z_R$) was 1.82mm. This enabled us to apply the thin sample approximation [23]. Figure 4.5 shows the nonlinear absorption traces of the dissolved compounds at typical beam energy of 0.83GW/cm$^2$. At this intensity, the open aperture Z-scan plot shown in Figure 4.5 shows no symptom of nonlinear absorption for IND-1, whereas for other samples, the OA trace looks like an inverted bell-shape which symmetrically extends to both sides of the focal plane at $z=0$. For the temporally and spatially Gaussian profiled pulses, the open aperture data of polyindole is found to be exactly fittable to the relation [24]:

$$T_{\text{open}}(z) = \left[ \frac{e^{-\alpha_0 L}}{q(z)\sqrt{\pi}} \right] \int_{-\infty}^{\infty} \ln\left[ I + q(z) e^{-r^2} \right] dt \quad (4.1)$$

where $q(z) = [\beta \frac{I_0}{L_{\text{eff}}}]/[1+(z/z_R)^2]$ and $L_{\text{eff}} = (1-e^{-\alpha_0 I_0})/\alpha_0$ with $L$ being the actual sample thickness, $\alpha_0$ the linear absorption coefficient at the far-field of the laser beam, $\beta_{\text{eff}}$ is the effective two-photon absorption coefficient, $I_0$ the beam intensity at the focal point, and $z_R = \pi w_0^2/\lambda$ is the Rayleigh range. The effective two-photon absorption coefficient, in fact, implies contribution from different mechanisms like two-photon absorption, reverse saturable absorption, thermally induced nonlinear scattering etc. We adopted this approach here firstly because the optical absorption spectra display a finite absorption at the excitation wavelength and secondly, there are inherent two-photon absorbing quantum levels in many of the IND molecules. An insightful approach will show that the effective intensity dependent nonlinear absorption in the samples is expressible in a form given by

$$\alpha(I) = \frac{\alpha_0}{I + 1/I_{\text{sat}}} + \beta_{\text{eff}} I \quad (4.2)$$

where, all the notations have their usual meaning as illustrated in Chapter 2.
Figure 4.5 Open aperture Z-scan traces of indole based molecules dissolved in DMSO. Pulse energy 30µJ/pulse, 7ns, 532nm. Merged trace shown at the bottom is for comparative estimation.

Open aperture data have been fitted to the relations shown in Equation 4.2 and the extracted linear and third order nonlinear optical parameters are listed in Table 4.1.
Table 4.1 Experimentally determined values of $T$, $n_0$, $n_2$, $\alpha_0$, $I_{\text{sat}}$, and $\beta_{\text{eff}}$ for different Indole compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>T</th>
<th>$n_0$</th>
<th>$\beta_{\text{eff}}$ (cm/GW)</th>
<th>$\alpha_0$ (cm$^{-1}$)</th>
<th>$I_{\text{sat}}$ (GW/cm$^2$)</th>
<th>$n_2$ ($\times 10^{-10}$ esu)</th>
<th>$\Delta\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IND-1</td>
<td>0.91</td>
<td>1.360</td>
<td>-</td>
<td>0.94</td>
<td>-</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>IND-2</td>
<td>0.44</td>
<td>1.453</td>
<td>89.0</td>
<td>8.19</td>
<td>0.075</td>
<td>-1.23</td>
<td>2.380</td>
</tr>
<tr>
<td>IND-3</td>
<td>0.56</td>
<td>1.442</td>
<td>64.0</td>
<td>5.75</td>
<td>0.071</td>
<td>-1.03</td>
<td>2.231</td>
</tr>
<tr>
<td>IND-4</td>
<td>0.54</td>
<td>1.442</td>
<td>62.0</td>
<td>6.13</td>
<td>0.072</td>
<td>-1.15</td>
<td>2.456</td>
</tr>
</tbody>
</table>

The above measurements reveal the potential of IND-2 as an efficient nonlinear absorber which yields the highest nonlinear absorption coefficient among the all the indole based compounds investigated. Figure 4.5 shows that IND-1 exhibits no symptom of intensity dependent absorption effects at the beam focal plane, whereas other compounds exhibit a phenomenal drop in transmittance at the focal point. Since Figure 4.3 shows that all samples are having slight linear absorption at the excitation wavelength, the actual dynamics may be an excited state absorption (ESA) mechanism [25]. Contribution also arises from two-photon absorption (TPA) mechanism due to the strong absorption at the vicinity of 266nm, which is twice the excitation frequency. This situation is an example of how linear absorption can promote the species to excited states that serve as the lower state of a second allowed transition before the excited state electron decay back to the ground state. ESA is the primary reason for transmission nonlinearity shown by many organic compounds when excited by nanosecond laser pulses [26]. In brief, the NLO behaviour in IND-2, 3, 4 molecules is due to the prevalence of both TPA and ESA mechanisms.

4.6.2 Closed Aperture (CA) Z-scan studies

The closed aperture Z-scan curves of IND samples are shown in Figure 4.6. IND-1 shows no variation in the normalized transmittance, which implies that the compound does not possesses any nonlinear refractive effect at the specified beam parameters. But, the rest of the compounds show appreciable variation in normalized transmittance for different sample positions. A peak-valley configuration of the CA trace is a manifestation of the negative optical nonlinearity of the samples [27].
Samples showing negative optical nonlinearity usually display self defocusing of the beam within the medium. The negative value of nonlinear refractive index implies that the overall refractive index of the sample tends to be less than what it possesses in the low intensity regime. Hence, the behaviour of the material is something like a concave lens of variable focal length. As a consequence to this, a Gaussian profiled beam propagating through the sample will experience the lowest refractive index near the beam axis and the highest at the beam periphery (where, $1/e^2$ of the Electric field $E_0$ at the beam axis exists). This lateral refractive index variation provides the sample with a self-defocusing effect. Estimated values of real and imaginary part of $\chi^{(3)}$ along with the absolute value using the equations given in Chapter 2 are listed in Table 4.2.

Figure 4.6 Closed aperture Z-scan curves for the samples IND-1, IND-2, IND-3 and IND-4. Nonlinear phase shift $\Delta \Phi_0$ of the samples are respectively 0, 2.38, 2.231, and 2.456.
Table 4.2 Experimentally determined values of $\text{Re} \chi^{(3)}$, $\text{Im} \chi^{(3)}$, total $\chi^{(3)}$ and figure of merit of the samples under 7ns, 532nm excitation

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta \Phi$ (x10^{-9} esu)</th>
<th>$n_2$ (x10^{-10} esu)</th>
<th>$\text{Re} \chi^{(3)}$ (x10^{-11} esu)</th>
<th>$\text{Im} \chi^{(3)}$ (x10^{-11} esu)</th>
<th>$\text{Tot} \chi^{(3)}$ (x10^{-11} esu)</th>
<th>$F$ (Z-scan) (x10^{-12} esu.cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IND-1</td>
<td>-</td>
<td>0</td>
<td>0.00</td>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>IND-2</td>
<td>2.380</td>
<td>-1.23</td>
<td>-1.90</td>
<td>2.02</td>
<td>2.77</td>
<td>3.38</td>
</tr>
<tr>
<td>IND-3</td>
<td>2.231</td>
<td>-1.03</td>
<td>-1.57</td>
<td>1.43</td>
<td>2.13</td>
<td>3.70</td>
</tr>
<tr>
<td>IND-4</td>
<td>2.456</td>
<td>-1.15</td>
<td>-1.76</td>
<td>1.39</td>
<td>2.24</td>
<td>3.66</td>
</tr>
</tbody>
</table>

The data listed in Table 4.2 indicate that the highest nonlinear phase shift is displayed by IND-4, but its nonlinear absorption coefficient is less than that of IND-2. IND-2 shows the highest nonlinear refractive index of -1.23x10^{-10} esu. This is because of the fact that the effective sample length is slightly higher for IND-4 than that of IND-2. In case of IND-3, the allyl moieties linked to the indole main ring has an explicit contribution in elevating the band gap (3.55eV). This, in turn, has improved the transparency factor of the solution. The increased Z-scan optical figure of merit of IND-3 can be accounted this way.

4.6.3 Closed by Open Aperture Z-scan studies

The peak-valley configuration of the pure nonlinear refraction curve, obtained by the division method is shown in Figure 4.7. The profile of the plots reveals self-defocusing property of the compounds, so, the sign of the nonlinear refractive index tends to be negative. The calculated values of third-order optical parameters of the samples are tabulated in Table 4.2. The $n_2$ and $\chi^{(3)}$ values are of the order of 10^{-10} esu and 10^{-11} esu respectively. This is comparatively higher than the values recorded by Ravindra et al in chalcones [28] and Kiran et al in certain thiophene derivatives [29]. Further, to determine the contribution of the solvent DMSO to the observed nonlinearity, we carried out Z-scan experiment on pure DMSO. It is observed that neither nonlinear refraction nor nonlinear absorption was observed at the input energy used. Hence, the contribution from the solvent to the optical nonlinearity of the samples is not coming in to the picture.
Figure 4.7 Pure nonlinear refraction curves of samples CM-2, CM-3 and CM-4 showing peak-valley configuration at 0.83GW/cm² beam intensity.

4.6.4 Investigation of nonlinear absorption mechanism in IND molecules

Generally, the nonlinear absorption can be caused by free carrier absorption, saturable absorption, direct multiphoton absorption, or excited state absorption [30]. If the mechanism belongs to the simple two-photon absorption, $\beta_{\text{eff}}$ should be independent of on-axis peak irradiance $I_0$. If the mechanism is direct three-photon absorption, $\beta_{\text{eff}}$ should be a linearly increasing parameter of $I_0$ and the intercept on the vertical axis must be nonzero. But the $I_0$ versus $\beta_{\text{eff}}$ plot of the samples presented in Figure 4.8 shows that $\beta_{\text{eff}}$ is decreasing with increasing $I_0$. This fall-off in effective two photon coefficient with increase in beam intensity is a consequence of reverse saturable absorption [31]. Figure 4.8 shows that all compounds exhibit RSA type behaviour under laser irradiance within the energy range of 0.75 to 2.5 GW/cm².
Figure 4.8 Input on-axis peak intensity ($I_0$) versus ($\beta_{eff}$) plot of compounds IND-2, IND-3 and IND-4 showing fall in the magnitude of effective two-photon absorption coefficient with increasing beam intensity. The data was taken at a concentration of 0.1(%m/v) for IND-2 and for other two compounds the concentration was set at 0.05(%m/v).

The change in intensity of the beam $I(z)$ as it propagates through the material is given by

$$\frac{dI}{dz} = -\alpha_{exc}I - \sigma_{exc}NI$$  \hspace{1cm} (4.3)

where $I$ indicates the beam intensity, $z$ the distance within the sample, $N$ the number density of molecules in the excited state, and $\sigma_{exc}$ is the excited state absorption cross-section. The excited state density of molecules appears as a result of nonlinear absorption process whose intensity dependence can be obtained from the relation [32]

$$\frac{dN}{dt} = \frac{\sigma_{exc}I}{h\nu}$$  \hspace{1cm} (4.4)
where, $\nu$ is the frequency of the laser. Combining Equations (4.3) and (4.4) and solving for the fluence of the laser and over the spatial extent of the beam gives the normalized transmittance $T(z)$ for open aperture as

$$T(z) = \ln \left[ 1 + \frac{q}{I + \left( \frac{z}{z_R} \right)^2} \right] / \left[ 1 + \left( \frac{z}{z_R} \right)^2 \right]$$

(4.5)

A fit of the open aperture data with the above relation will yield the values of the excited state cross sections of the samples for 532nm wavelength and 0.83GW/cm$^2$ beam intensity, where $q$ is given by the $q=(\sigma_{exc} \alpha F_L L_{eff})/2h\nu$. Here, $F_0$ is the fluence of the laser at the focus ($z=0$).

**Table 4.3. Molecular Second hyperpolarizability ($\gamma_h$), Ground and excited state absorption cross-sections for Indole-based systems at 532nm, 0.83 GW/cm$^2$ beam intensity.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\gamma_h$ (x$10^{-30}$ esu)</th>
<th>$\sigma_{grd}$ (x$10^{-18}$ cm$^2$)</th>
<th>$\sigma_{exc}$ (x$10^{-17}$ cm$^2$)</th>
<th>$\sigma_{exc}/\sigma_{grd}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IND-1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>IND-2</td>
<td>12.5</td>
<td>13.1</td>
<td>5.17</td>
<td>3.96</td>
</tr>
<tr>
<td>IND-3</td>
<td>7.10</td>
<td>6.56</td>
<td>4.80</td>
<td>7.31</td>
</tr>
<tr>
<td>IND-4</td>
<td>8.42</td>
<td>7.87</td>
<td>2.18</td>
<td>2.77</td>
</tr>
</tbody>
</table>

Similarly, the ground state absorption cross section $\sigma_{grd}$, can be calculated from the expression $\sigma_{grd}=\alpha/N_A C$, where $N_A$ is Avogadro’s number and C is the concentration in moles/cm$^3$ [24]. For measuring the molecular weight of the polymers, we used MALDI (Matrix-Assisted Laser Desorption/Ionization Mass spectrometry experiment) technique outlined in Chapter 5. Molecular weight of the molecules as obtained from MALDI output for IND-2, IND-3 and IND-4 are given by 480.25, 343.82 and 386.49 respectively. These values show that indole does not form giant polymeric systems; instead, they form oligomers with medium molecular weight. The ground state absorption cross-section of IND-2 is
13.1\times10^{18}\text{cm}^2\) whereas, it’s excited state absorption cross section is \(5.17\times10^{17}\text{cm}^2\). This is a favourable condition (\(\sigma_{\text{exc}} > \sigma_{\text{grad}}\)) for reverse saturable absorption to take place [33]. Similar cross-sectional values are obtained for other compounds as well (Except in IND-1, which hardly showed any NLO response) and are presented in Table 4.3.

### 4.6.5 Concentration dependence of nonlinear absorption

For concentration dependence measurements, molecular solutions with typical concentrations of four different weight percent were prepared. The solutions were checked to detect the presence of undissolved solute components and ensured the homogeneity of the solutions with UV-Vis spectrometer and microscope. This is an essential procedure because, often, due to insufficient stirring, polymers are likely to form agglomerated grains in DMSO which may lead to induced scattering. Often, this nonlinear scattering may be misinterpreted as the consequence of nonlinear absorption [33].

**Figure 4.9 a)** Concentration dependence of nonlinear absorption coefficient for IND-2 and IND-4. Transmittance percentage at different concentrations is also appended.

**Figure 4.9 b)** The open aperture Z-scan trace of IND-2 for different solute concentrations in DMSO taken at beam energy of 30\(\mu\text{J/pulse}\).

Concentration dependence of NLO coefficients can be analyzed to extract information on the nonlinear optical properties of the solute. Figure 4.9 a) shows the plot of the nonlinear absorption coefficient versus dopant concentration in the compounds IND-2 and IND-4. Similar behaviour was observed for IND-3 as well. The graph shows that the measured values of the nonlinear absorption coefficient \(\beta_{\text{eff}}\) increases almost linearly with the concentration of the sample in DMSO. We could not observe any saturation behaviour for
NLA or NLR within the entire range of concentrations that we used. The nonlinear refraction was also found to increase with increasing concentration. This trend indicates that the contribution to NLO properties arises from the nonlinearity of the polymers.

4.6.6. IND-2 : GRAPHENE OXIDE COMPOSITES IN DMSO

It is well reported by many researchers that combining graphene oxide with organic conjugated polymers would facilitate the enhancement of nonlinearity [35-37]. Exfoliated GO sheets are a form of graphene and are very suitable for chemical processing. GO is a two dimensional network of small sp² carbon clusters isolated by sp³ bonded carbon matrix, resulting in a heterogeneous electronic structure that features both π-states from the sp² carbon sites and large energy gap between the σ-states of the sp3 carbons. The large scale optical nonlinearity of graphene oxide (GO) has been proved to be useful in a number of photonic device applications. In the present work, IND-2 was combined with GO in different proportions and their NLO behaviour was investigated by giving thrust on optimizing transparency and NLA parameters (See Figure 4.10). At moderate concentration, GO is not fairly transparent in the visible region.

Further, GO is sparingly soluble in many organic solvents but its NLO coefficients are very high. In DMSO, we found that it is almost completely soluble under ultrasonication. On the

![Figure 4.10](image-url)  
**Figure 4.10.** The plot (violet lines) explains the variation of \( \beta_{\text{eff}} \) with increasing proportions of GO. The variation of linear transmittance with increasing amount of graphene is shown with pink line. The optimized value of transmittance and nonlinear absorption coefficient is given by the intersecting point. The ‘PIN’ shown in the graph means IND-2.

Further, GO is sparingly soluble in many organic solvents but its NLO coefficients are very high. In DMSO, we found that it is almost completely soluble under ultrasonication. On the
other hand, IND-2 is completely soluble in DMSO and its transparency is fairly good. By combining the properties of these compounds we expect to form a hybrid one with improved transparency and optimized NLO coefficients. In the present work, GO has been prepared by the modified Hummer’s method [38] through the acid oxidation of flake graphite and was characterized by UV-Vis spectroscopy to observe the characteristic peaks. Figure 4.10 depicts the variation of $\beta_{\text{eff}}$ with different concentrations of IND-2/GO solutions.

![Figure 4.10](image)

**Figure 4.10** Variation of $\beta_{\text{eff}}$ with different concentrations of IND-2/GO solutions.

The stock solution of GO at an initial concentration of 4mg/4ml was prepared by dispersing GO in DMSO using a sonicator and the dispersion quality was checked by visual method using microscope and absorption spectroscopy to verify the homogeneity of the solution. IND-2/GO mixture solutions were prepared by adding IND-2 solutions of different mass percentage into a fixed volume of prepared standard GO solution. Figure 4.11 shows the absorption spectrum of GO and its composites made with IND-2 in different ratios. The bathochromic shift of the absorption peak with increasing proportions of IND-2 is a favourable factor for enhancing nonlinearity in the composite.

![Figure 4.11](image)

**Figure 4.11** UV-Vis absorption spectra of GO/IND-2 compositions. Spectra show the bathochromic shift of GO/IND-2 composite peak with increasing percentage of IND-2.
The open aperture Z-scan plots of the prepared solutions are shown in Figure 4.12. OA Z-scan plots depicts the variation of NLA with varying proportions of GO. Associated NLO parameters extracted by fitting the Z-scan data with the theoretical relations illustrated in Chapter 2 is presented in Table 4.4.

**Table 4.4 Measured NLO parameters for GO/IND-2 composites at 532nm, 0.83 GW/cm$^2$ beam intensity**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample Composition</th>
<th>Linear Transmittance</th>
<th>$I_{\text{Sat}}$ (10$^{-3}$ GW/cm$^2$)</th>
<th>$\beta_{\text{eff}}$ (cm/GW)</th>
<th>$\text{Im} \chi^{(3)}$ (10$^{-11}$ esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>IND-2:GO (1.0 : 0.0)</td>
<td>34.59</td>
<td>79.99</td>
<td>120</td>
<td>2.72</td>
</tr>
<tr>
<td>2.</td>
<td>IND-2:GO (1.5 : 0.5)</td>
<td>31.27</td>
<td>59.99</td>
<td>171</td>
<td>3.88</td>
</tr>
<tr>
<td>3.</td>
<td>IND-2:GO (1.0 : 0.5)</td>
<td>29.50</td>
<td>59.99</td>
<td>151</td>
<td>3.37</td>
</tr>
<tr>
<td>4.</td>
<td>IND-2:GO (0.5 : 0.5)</td>
<td>29.27</td>
<td>50.00</td>
<td>170</td>
<td>3.79</td>
</tr>
<tr>
<td>5.</td>
<td>IND-2:GO (0.0 : 1.0)</td>
<td>11.54</td>
<td>55.00</td>
<td>410</td>
<td>9.26</td>
</tr>
</tbody>
</table>

We could obtain an optimization in terms of transparency and $\beta_{\text{eff}}$ by extrapolating the graph (See Figure 4.10). An optimized value of 275cm/GW can be obtained for $\beta_{\text{eff}}$ at a
concentration of IND-2/GO (4.5:0.5) with a projected transparency of 22.50% at the given excitation wavelength and pulse width. Here, the open aperture Z-scan and UV-Vis results indicate that certain interaction kinetics has come into action between GO and polyindole oligomers. The shifting of absorption maximum in UV-vis spectrum is also an supporting indication of the same assumptions. An enhancement in the nonlinear absorption at certain composition is clear from the obtained results and that could be due to an interplay of various mechanisms like ESA, RSA, TPA and NLS with energy transfer between GO and polyindole (IND-2) molecules. Similar strategy was tried with other compounds as well. But, the response was comparatively poorer than what we obtained for IND-2. It demands to redesign the strategy for rest of the compounds.

4.6.7. Structure-Property Relationship

Enhanced conjugation mechanism in IND-2, 3 and 4 molecules may be interpreted as follows. Chemical bonding in polyindole provides one unpaired electron per atom, that is, one \( \pi \)-electron per carbon atom in the backbone of the polymer. Carbon atoms are in \( sp^3p_z \) configuration in \( \pi \)-bonding. One valence electron per each carbon centre resides in a \( p_z \) orbital, which is orthogonal to the other three \( \sigma \)-bonds. All the \( p_z \) orbitals combine with each other in a molecule via delocalized set of orbitals. Orbitals of successive carbon atoms overlap each other providing delocalization of electrons along the molecular backbone of the polymer [39-41]. This delocalization provides the charge mobility along the backbone of the polymer chain and induces unusual properties such as electrical conductivity, low ionization potential, low energy optical transitions, and high electron affinity. The origin of electrical conduction in conducting polymers like the IND series discussed here has been ascribed to the formation of nonlinear defects such as solitons, polarons, or bipolarons [42, 43] formed during either doping or polymerization of a monomer.
Figure 4.13 Schematic representation of possible charge transfer mechanism taking place in indole oligomeric systems. Electron mobilization path is shown with red curly arrows.

The title compound IND-1 has been conjugated with large number of benzene and pyrene rings via in-situ polymerization. This process facilitates it with large number of delocalized $\pi$-electrons in the molecular backbone. This is more relevant from the perspective that polymerization of indole usually takes place more or less in a linear configuration as outlined in references [15-17] than in a lateral or three dimensional pattern. This property enables them to have increased charge transfer tendency across the molecular backbone and hence better interaction effects with the incident laser field, which is reflected in its enhanced optical nonlinearity. The presence of highly electronegative nitrogen atom within the molecular backbone of indole impedes the delocalization of electron in its ring structure, whereas, in IND-2, 2-2 and 3-3 linkages (see FTIR interpretations in Section 4.3) between neighbouring indole (IND-1) monomers facilitates easy electron mobilization and hence attains extended conjugation along the entire polymer (oligomer) structure [44] as shown in Figure 4.13. Pendant-styled orientation of indole monomers along the PIN backbone contribute to additional mobilisation to the delocalized electrons whereby electrons opt to migrate through non-nitrogen occupying routes.
In IND-3 allyl moiety is attached to the 2-position. The presence of delocalizing double bonds in the allyl moiety facilitates charge mobilization and this trend is also obvious from the bathochromic shift of IND-3 with respect to IND-1 (see linear absorption spectra given in Section 4.3). Moreover, IND-3 shows appreciably good nonlinear absorption and refraction. Another added advantage is that IND-3 displays improved transparency compared to IND-2 which is accountable with its broadened band gap (~3.55eV) value. In case of IND-4, the band gap is found to be much reduced than IND-3; the possible reason could be the presence of benzyl moiety which is more of a donor-like.

4.6.8 IND/PMMA Films

Thin films of IND-2 and IND-3 were fabricated on microscope glass slides (C-Poulo Labtech) as per the procedure outlined in Chapter 4. Thickness and surface evenness were verified and linear refractive index measured with ellipsometric technique.

(a) Open aperture Z-scan trace of IND-2 at 0.83 GW/cm² intensities.
(b) Open aperture of IND-3 at 0.83 GW/cm² beam intensity.
(c) Open aperture Z-scan trace of IND-3 at 0.28 GW/cm² beam intensity.

Figure 4.14 Open aperture Z-scan traces of Indole derivatives with IND-2 and IND-3 doped in PMMA matrix. Plots are given for different beam intensities.
Open aperture Z-scan traces of IND/PMMA thin films showed entirely different type of absorption behaviour. In solution phase all samples displayed RSA behaviour with a sharp fall in transmittance at the focal plane. On the other hand, in thin film form, IND-2 exhibited saturable absorption behaviour at 10, 30, 60 µJ pulse energies. For 30 µJ pulse, IND-2 yielded an SA peak which corresponds to a NLA coefficient value of $-7.4 \text{cm/GW}$. We analyzed the film up to a beam intensity of $2.5 \text{GW/cm}^2$. We couldn’t observe any change in the nonlinear absorption behaviour other than SA. On enhancing the beam intensity beyond this value on the film, it started to form damaged patches, while in IND-3, the response pattern was entirely different. For 10µJ pulse, sample yielded RSA response with a $\beta$ value of $64 \text{cm/GW}$ ($I_{\text{sat}}=14.5 \times 10^{10} \text{W/m}^2$), whereas at 30µJ, the response was entirely SA with an NLA coefficient of $-1.55 \text{cm/GW}$. The fundamental physical mechanism for this sudden switching response is ascribable to the changes in the lifetime ($\tau$) of the excited states [45]. In case of IND-2, at high input intensities, excited states are quickly saturated and hence no more absorption takes place beyond certain threshold input intensities. So, the sample begins to display optically induced transparency. Similar is the case with IND-3 also (with an exemption that at low input irradiance ~ 0.3 GW/cm$^2$, it exhibits RSA behaviour). Possible reason for this effect could be hypothesized as follows. In thin solid film form, at low irradiance, excited states do not get readily saturated hence the system follows RSA type of mechanism, at higher irradiance, most of the molecules go either to higher excited singlet states or to long-lived triplets, resulting in a depleted ground state leading to the so-called saturable absorption. This delay mechanism renders the film specimen a saturated type of absorption mechanism at higher irradiance (>0.3 GW/cm$^2$) conditions making them suitable for efficient laser pulse narrowing applications.

4.7 OPTICAL LIMITING

In general, as mentioned in Chapter 2, an ideal optical limiter display constant normalized transmittance at low input fluences and a highly reduced sharp fall in transmittance beyond a predetermined input fluence. In good optical limiters the limiting action is instantaneously activated by the input flux, provided its value exceeds the threshold energy prescribed for the material. Beam irradiance then initiates the absorptive and refractive properties in the materials in such a way that the emerging beam intensity will be substantially reduced. This phenomenon finds applications in pulse shaping, pulse
compression, mode locking and direct viewing optical systems. Various mechanisms like 2PA, 3PA, ESA, RSA, free carrier absorption and optically induced heating etc make their interplay in inducing optical limiting action in materials [46-48].

In the present work, the compound IND-1 shows no kind of liming action at the entire range of beam energies whereas it’s polymerized versions namely, IND-2, IND-3 and IND-4 display (Figure 4.15) excellent optical liming property.

**Figure 4.15** Optical power limiting characteristic curves of IND series of compounds. Figure 4.15 (e) represents the comparative performance of all the samples where the upper X-axis shows the input fluence in J/cm².
As depicted in Figure 4.15 a) IND-1 does not show any symptoms of optical limiting. But OL plot of IND-2 shown in Figure 4.15 b) indicates that the normalized transmittance at different beam input intensities and it can be observed that normalized transmittance \( T(z) \) has been phenomenally got reduced (~50%) for input intensities greater than 0.027GW/cm\(^2\). Similarly, IND-3 and IND-4 also showed similar properties beyond 0.030 and 0.035GW/cm\(^2\) respectively.

Usually performance of an optical limiter is scaled based on its \( T_H \) value [49]. It is the input energy at which the transmittance becomes 50% of the low beam-intensity transmittance. The lower the \( T_H \), the better is the performance of a particular optical limiter. In case of IND-2, its \( T_H \) is 0.27GW/cm\(^2\) which is a low value compared to the \( T_H \) of many standard organic compounds like phthalocyanines as reported by Mathews et al. [50]. Similar observations were made by Wang et.al [51] in graphene oxide-carboxymethyl cellulose composite films. No literature report has been found so far where IND-2 or any of its other derivatives discussed here being used as an optical limiter.

4.8 PHOTOLUMINESCENCE (PL) STUDIES

In order to study the emission features of indole derivatives, photoluminescence (PL) spectra of the compounds dissolved in DMSO were recorded at room temperature by exciting with appropriate wavelengths obtained from UV-Vis plots and is shown in figure 4.16. PL spectrum is a great source of information about the pathways that a molecular system evolves during its de-excitation to the ground state. The possible pathways include fluorescence and nonradiative internal conversion processes. The latter is less probable in a smooth, homogeneous solvent medium like DMSO.
A strong emission peak was observed for IND-1 at 327nm, whereas that for IND-2, it has got largely broadened with respect to that of indole, and lies at 438.37nm. There are two auxiliary emission peaks for IND-2, which are positioned at 414.5nm and 463nm respectively. Relative peak intensity depends on the corresponding radiation quantum efficiency of the level involved. Lorentzian-Gaussian (L-G) fit [52] (Figure 4.16 b)) on the PL spectra of IND-2 yield three visible emission peaks whose composition is as follows:

**Figure 4.16** Deconvoluted photoluminescence spectra of indole (IND) derivatives
\( \lambda_1 = 467.12\text{nm} \) (55.94\%), \( \lambda_2 = 438.37\text{nm} \) (37.99\%) and \( \lambda_3 = 410.57\text{nm} \) (6.06\%). Meanwhile, L-G fit on IND-1 spectra (Figure 4.16 a)) shows the following composition: \( \lambda_1 = 348.54\text{nm} \) (35.07\%), \( \lambda_2 = 328.8\text{nm} \) (43.18\%) and \( \lambda_3 = 313.47\text{nm} \) (21.74\%). For IND-3 the composition is: \( \lambda_1 = 444.85\text{nm} \) (56\%), \( \lambda_2 = 520.9\text{nm} \) (43.9\%); and for IND-4, it is given by: \( \lambda_1 = 415\text{nm} \) (20.5\%), \( \lambda_2 = 441\text{nm} \) (35.6\%) and \( \lambda_3 = 465.5\text{nm} \) (43.9\%). Obviously, the dominant part of the emission for IND-1 falls in the UV region (200nm-380nm) whereas that of the other three compounds wholly lies in the visible region [53]. The polymers like IND-2, IND-3 etc, emitting in the visible band of the spectrum can be considered as a material of immense potential, as they can offer stable sources of light for displays and illumination purposes at an appreciably lower cost than the semiconductors or other crystalline photonic materials [54]. It can be noted that the enhanced conjugation via polymerization has resulted to cause red shift in the PL spectra of the last three compounds compared to the first sample IND-1.

4.9 CONCLUSION

Various indole based oligomeric molecular systems were synthesized by in-situ chemical oxidative polymerization method using ammonium peroxydisulfate as oxidant and the characteristic bond formation of the obtained compounds have been inferred with FT-IR spectroscopy. Linear absorption features of all the four compounds were studied with optical absorption spectra. All compounds except CM-1 exhibit finite linear absorption at the excitation wavelength 532nm. Deconvoluted PL spectrum of the derived compounds display distinct emissions features which falls in the visible part of the electromagnetic spectrum. Open aperture Z-scan traces of compounds IND-2 to IND-4 revealed RSA nonlinearity, predominantly attributable to ESA with contribution from two-photon absorption as well. Closed aperture Z-scan traces of all derived samples show a peak-valley profile which is a signature of negative nonlinear refractive index and hence attributable to the self-defocusing behaviour of the compounds. Meanwhile, IND-1 molecule did not show either nonlinear absorption or nonlinear refraction at the applied beam energies and pulse width. Polymers also show reasonably good optical limiting efficiency with low \( T_H \) values and is found to be improving with increasing concentration of the solute molecules indicating its potential applications in optical power limiters used in direct viewing systems. The structure-property relationships of the molecules were explained. Two of the samples were studied in its thin film form by doping in PMMA matrix. In thin film form, samples were mostly exhibiting saturable type of absorber behaviour. In Chapter 7 of this report, we will see the nonlinear response of these molecules in the femtosecond time domain.
REFERENCES


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