Chapter 6

Novel Soluble Phenothiazine-Triazine Copolymer: Synthesis and Third-order Non-linear Optical Properties

Abstract

Novel soluble conjugated phenothiazine-N-piperidine substituted triazine copolymer, (P(PH-TZ)) has been designed and synthesized via Suzuki coupling reaction. The electronic properties of the copolymer were investigated by employing density functional theory (DFT) in the periodic boundary condition (PBC) formalism at HSE06 and B3LYP level of theory. The copolymer showed good solubility in common organic solvents like chloroform, tetrahydrofuran and chlorobenzene. Polymer showed broad absorption spectrum with wavelength maximum at 395 nm with optical band gap of 2.5 and 2.3 eV in THF solution and as thin film, respectively. The theoretically calculated values were in good agreement with experimental results. In thin film, the energy gap tends to narrow and the absorption and emission peaks are red shifted to longer wavelengths due to the increase in planarity of the copolymer in thin film. The copolymer, P(PH-TZ) showed third-order non-linear optical susceptibility and optical limiting threshold of $1.27 \times 10^{-11}$ esu and 0.22 GW/cm², respectively.
6.1. Introduction

Organic π conjugated structures with 1,3,5-triazine as the core unit have received significant attention due to their promising applications in liquid crystalline materials,1,2 magnetic materials,3 solar cells4-6 and light-emitting diodes (LEDs).7,9 Owing to their high thermal stability, polymers containing 1,3,5-triazine unit are widely used in industry. Recently, some new polymers bearing 1,3,5-triazine units have been reported.8-11 The 1,3,5-triazine unit possesses high electron affinity,12 structural symmetry, high thermal, mechanical and oxidative resistance.13-17 Unfortunately, these features also lead to low solubility and processability. Insertion of phenothiazine unit with bulky alkyl substituent imparts flexibility to this copolymer. The 1,3,5-triazine unit in the polymer backbone favoured the better electron injection and transportation in devices.7,8

Phenothiazines are a class of electron rich tricyclic nitrogen-sulphur heterocycle compound with low oxidation potential, high luminescence and photoconductivity. They are widely used as dyes, antioxidants, pharmaceuticals etc.18,19 These molecules are potential candidates for applications in LEDs,20-22 photovoltaic devices23-26 and organic field effect transistors.27,28 The π conjugated organic compounds have emerged as promising candidates due to their fast response time, large third-order susceptibility and processability.29,30 The NLO properties of organic molecules can be tuned by adopting suitable synthetic strategies, such as donor–π–acceptor (D–π–A), donor–π–donor (D–π–D), donor–acceptor–donor (D–A–D), and acceptor–donor–acceptor (A–D–A).31,32 Here, we are mainly interested in the alternating donor-acceptor copolymer since their optoelectronic properties
can be tuned by efficient intramolecular charge transfer. The strong donor-acceptor intramolecular interaction and delocalized \( \pi \)-electron system yields NLO properties in \( \pi \) conjugated organic compounds. This in turn intrigued our research interest in the third-order NLO behaviour of D-\( \pi \)-A type copolymer, P(PH-TZ). In this paper, we discuss the electronic structure, synthesis, optical and electrochemical properties of phenothiazine-triazine copolymer and have demonstrated the applicability of the polymer as active material in optical limiting devices.

6.2. Results and discussion

6.2.1. Theoretical calculation

All the DFT\textsuperscript{33} calculations were carried with Gaussian 09\textsuperscript{34} program. The monomer geometries were optimized by B3LYP/6-31G method.

![LUMO and HOMO](image)

*Fig. 6.1: Frontier molecular orbital distribution of monomeric unit of P(PH-TZ) by B3LYP/6-31G method.*
Fig. 6.1 shows the frontier molecular orbitals of monomeric unit, PH-TZ. It reveals that the HOMO (highest occupied molecular orbital) level of PH-TZ was located on phenothiazine unit and LUMO (lowest unoccupied molecular orbital) level was located on triazine moieties. This large degree of polarization might be responsible for the small band gap value for P(PH-TZ) compared to homopolymer, poly(phenothiazine) (P(PH)).

The electronic properties of the P(PH) and P(PH-TZ) were studied by PBC calculation at two different energy levels (B3LYP\textsuperscript{35-37}/6-31G and HSE06\textsuperscript{38,39}/6-31G) and the band structure obtained by HSE06/6-31G level have been plotted in Fig. 6.2. Table 6.1 lists the calculated theoretical HOMO-LUMO energy levels and band gaps of the homopolymer, (P(PH)) and copolymer, P(PH-TZ).

![Fig. 6.2: Band structure of P(PH-TZ) by HSE06/6-31G method.](image)

Comparing the band structure of P(PH-TZ) with band structure of P(PH), it could be seen that energy of HOMO level of P(PH) was lowered...
by a factor of 0.13 eV while LUMO level was lowered by a factor of 0.61 eV and we get P(PH-TZ) with a reduced band gap of 2.87 eV. The lower band gap of P(PH-TZ) compared to that of P(PH), indicated a significant effect of intramolecular charge transfer between the phenothiazine and triazine moieties.

Table 6.1: Computational data of P(PH) and P(PH-TZ) with DFT/B3LYP/6-31G and DFT/HSE06/6-31G methods.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(PH)</td>
<td>-4.76</td>
<td>-1.41</td>
<td>3.35</td>
</tr>
<tr>
<td>P(PH-TZ)$^a$</td>
<td>-5.02</td>
<td>-1.75</td>
<td>3.27</td>
</tr>
<tr>
<td>P(PH-TZ)$^b$</td>
<td>-4.89</td>
<td>-2.02</td>
<td>2.87</td>
</tr>
</tbody>
</table>

$^a$Obtained by the DFT/B3LYP/6-31G method, $^b$Obtained by the DFT/HSE06/6-31G method.

6.2.2. Synthesis and Characterization

The synthetic procedures towards the synthesis of monomers and copolymer are outlined in Schemes 1 and 2. Scheme 1 summarizes the synthesis of key monomers. The monomer 2-(N-piperidine)-4,6-dichloro-s-triazine (3) was synthesized from cyanuric chloride (1) and piperidine (2) in acetone according to standard procedure. The monomer, 10-octyl-3,7-bis(4,4,5,5-tetramethyldioxaborolan-2-yl)-phenothiazine (7) was synthesized in three steps starting from the phenothiazine (4). Firstly, 10-octylphenothiazine (5) was synthesized by the alkylation of phenothiazine (4) using 1-bromoocctane and KOH. 3,7-Dibromo-10-(octyl)-phenothiazine (6) was prepared by brominating the 10-octylphenothiazine in CH$_2$Cl$_2$. To obtain 10-octyl-3,7-bis(4,4,5,5-tetramethyldioxaborolan-2-yl)-phenothiazine (7), 3,7-dibromo-10-(octyl)-phenothiazine (6) was stirred with n-butyl lithium followed by 2-isopropoxy-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane in THF at -78 °C according to standard procedure.
Scheme 1: Synthesis of monomers.

The conjugated polymer derived from phenothiazine and triazine was synthesized by palladium (0) catalysed Suzuki coupling reaction with an equivalent ratio of diboronyl phenothiazine monomer (7) and 2-(N-piperidine)-4,6-dichloro-s-triazine monomer (3) using freshly prepared palladium triphenylphosphene as the catalyst. The copolymer was purified by washing with methanol and hexane in a soxhlet apparatus to remove the oligomers and catalyst residues and was dried under reduced pressure. After purification, the polymer was obtained in good yield (60 %).

Scheme 2: Synthesis of copolymer, P(PH-TZ).
The copolymer was readily soluble in common organic solvents, such as THF, chloroform, dichloromethane and chlorobenzene. The molecular weight of polymer was determined by gel permeation chromatography in THF referring to polystyrene standards. GPC analysis showed that copolymer had number average molecular weight (Mn) of 3580, weight average molecular weight (Mw) of 4928 and polydispersity index (PDI) of 1.66.

The molecular structure of the copolymer was verified by FT-IR, $^1$H NMR and XPS analysis. A representative FT-IR spectrum of triazine copolymer is shown in Fig. 6.3, where the bands at 805 and 1492 cm$^{-1}$ are attributed to the out of plane vibrations of 1,3,5-triazine ring. The intense bands at 1570 and 1539 cm$^{-1}$ are attributed to the aromatic C=C stretching of phenothiazine moiety. The aliphatic C-H stretching vibration appeared at 2931 and 2852 cm$^{-1}$ is an indication of alkylated phenothiazine moiety. The
copolymer also exhibited two bands at 905 and 983 cm\(^{-1}\) due to C-C deformation of piperidine ring. FT-IR results clearly indicated that copolymerization was successfully achieved.

![Fig. 6.4: \(^1\)H NMR spectrum of P(PH-TZ).](image)

The \(^1\)H NMR spectrum of P(PH-TZ) copolymer is depicted in Fig. 6.4. The \(^1\)H NMR spectrum showed multiplets at \(\delta\ 0.65-1.9\ ppm\) due to alkyl protons of phenothiazine and piperidine units and the characteristic signal of CH\(_2\) segments attached to the nitrogen atoms of phenothiazine and piperidine units was observed as multiplet at \(\delta\ 3.8\ ppm\). The peaks corresponding to aromatic protons of phenothiazine units were observed at \(\delta\ 6.8-7.5\ ppm\) as multiplets.
Fig. 6.5: XPS survey scan of P(PH-TZ) showing the presence of N1s, C1s, S2s, S2p and Si2p peaks.

Fig. 6.5 represents the XPS survey scan of the copolymer, P(PH-TZ) which showed the presence of C, N, S as the characteristic elements of the comonomers. In XPS spectrum, the signals related to C1s are observed at 282 eV, which is mainly due to aromatic carbons of the polymeric conjugated backbone. The N1s signal appear at 396 eV and is attributed to the presence of C-N bonding. The 2s and 2p core levels of S atom show signals at 228 and 160 eV, respectively, which reveals that monomeric units containing phenothiazine rings are present in the copolymer, as expected. The FT-IR, 1H NMR and XPS spectra of P(PH-TZ) are consistent with the chemical structure.

6.2.3. Photophysical properties

The photophysical characteristics of copolymer were investigated by both UV-Visible absorption (Fig. 6.6) and photoluminescence (PL) (Fig. 6.7) spectra in dilute THF solution and as thin film. As shown in Fig. 6.6, copolymer exhibited two distinct peaks and one of the peak appeared at
304 nm which is assigned to the $\pi-\pi^*$ transition and the other peak at longer wavelength at 395 nm, with tailing of absorption to around 496 nm can be attributed to the intramolecular charge transfer between the donor and acceptor unit. In thin film, copolymer exhibited two absorption bands at 294 and 410 nm, which are assigned to the $\pi-\pi^*$ transition and intramolecular charge-transfer, respectively. The thin film absorption pattern of P(PH-TZ) is nearly identical to the dilute solution spectrum, with red shifted absorption maximum of 425 nm.

![UV-Visible spectra of copolymer, P(PH-TZ) in (a) THF solution and (b) as thin film.](image)

Fig. 6.6: UV-Visible spectra of copolymer, P(PH-TZ) in (a) THF solution and (b) as thin film.

The optical band gap of P(PH-TZ) was calculated to be 2.5 eV, from the cut-off wavelength of optical absorption in THF solution. Optical band gap derived from the absorption edge of the polymer film was 2.3 eV, differed 0.2 eV, from the solution band gap. As expected, the copolymer has lower band gap than the conjugated homopolymer, poly(phenothiazine) (2.76 eV)\textsuperscript{41} due to better charge transfer between the units. Even if the optical band gap of copolymer showed good agreement with the theoretical
prediction (DFT/HSE06), some deviations still exists. This could be due to negligence of solid-state effects (polarization effects and intermolecular forces) and environmental effects in theoretical prediction.\textsuperscript{44,45}

![Graph showing PL spectra of copolymer, P(PH-TZ) in THF solution and as a thin film.]

**Fig. 6.7: PL spectra of copolymer, P(PH-TZ) in (a) THF solution and (b) as thin film.**

The PL emission maximum of P(PH-TZ) in THF solution and film are observed at 529 and 535 nm, respectively (Fig. 6.7). The absorption and emission peaks of P(PH-TZ) film show red shift in wavelength maximum compared to those obtained in the solution, which is caused by intermolecular interaction in thin film. Here, the copolymer emits in the green region, whereas its homopolymer emits in blue region (486 nm).\textsuperscript{41} The observed Stokes shift according to poly(phenothiazine) emission suggests that there is an intramolecular charge transfer between the phenothiazine and neighbouring triazine units.

### 6.2.4. Thermal properties

The thermal stability of copolymer was investigated by TGA and DSC under nitrogen atmosphere. The TG thermogram is depicted in Fig. 6.8. The
thermogram of the copolymer revealed that 5 W% loss was observed at 201 °C, which is an indication of moderate thermal stability. The thermal induced phase transition behaviour of copolymer was investigated with DSC under nitrogen atmosphere. The insert picture in Fig. 6.8 shows the DSC trace of the copolymer, P(PH-TZ). As for DSC trace, the copolymer exhibited no obvious phase transition until 250 °C, which is sufficient for device applications. The lower thermal stability of P(PH-TZ) in comparison with P(PH) (320 °C)\(^{41}\) could be due to the presence of piperidine units, which are highly prone to degradation.

Fig. 6.8: TG (a), DTG (b) and DSC (c) curves of copolymer, P(PH-TZ).

6.2.5. Electrochemical characterization

Electrochemical investigations of the copolymer were performed by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). To determine the HOMO and LUMO energy levels of the polymer, CV and DPV were carried out in thin polymer film which was coated on Pt electrode using 0.1M \(\text{Bu}_4\text{NPF}_6\) electrolyte in acetonitrile. The HOMO and LUMO
energies of the polymer were calculated from the onset values of the first oxidation and reduction peaks of CV and DPV using Bredas equation.\textsuperscript{46} The onset of oxidation occurs at 0.82 and 0.69 V in CV and DPV corresponding to HOMO energies of -5.22 and -5.09 eV, respectively. Similarly, onset of reduction occurs at -1.61 and -1.41V corresponding to LUMO energies of -2.99 and -2.79 eV for CV and DPV, respectively. The electronic properties of the copolymer are summarized in Table 6.2. Hence the electrochemical band of P(PH-TZ) was obtained to be 2.43 and 2.1 eV from CV and DPV, respectively. The band gap obtained from DPV is found to be smaller than CV values, because of reduced back current and sharper onset. The HOMO level of P(PH) was reported to be -5.0 eV.\textsuperscript{41} It is clear that the HOMO level of copolymer was lowered by 0.22 eV. This indicates that triazine unit is a strong electron acceptor due to the presence of more number of nitrogen atoms.

Table 6.2: Redox properties of copolymer, P(PH-TZ).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(PH)$^a$</td>
<td>-5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P(PH-TZ)$^b$</td>
<td>-5.22</td>
<td>-2.99</td>
<td>2.43</td>
</tr>
<tr>
<td>P(PH-TZ)$^c$</td>
<td>-5.09</td>
<td>-2.79</td>
<td>2.10</td>
</tr>
</tbody>
</table>

$^a$Reproduced from ref. 41, $^b$Obtained by CV, $^c$Obtained from DPV.

6.2.6. Non-linear optical (NLO) properties

The measurement of third-order NLO properties of copolymer, P(PH-TZ) was performed with the z-scan technique at 532 nm by the reported method.\textsuperscript{47} The open-aperture (OA) z-scan signal in dilute CHCl$_3$ is shown in Fig. 6.9.
Fig. 6.9: Open aperture z-scan trace of P(PH-TZ).

The normalized transmittance valley of light at the focus suggests that the copolymer is reverse saturation absorber (RSA) with positive NLO absorption coefficient. The non-linear optical absorption coefficient, $\beta$ is obtained by fitting the experimental data using equation (1)$^{47}$ (equation (3), given in section 2.2.7). The imaginary part of the third-order susceptibility (Im$\chi^{(3)}$) of P(PH-TZ) is determined by equation (2)$^{47}$ (equation (4), given in section 2.2.7). To determine the sign and magnitude of non-linear refraction, closed aperture (CA) z-scan$^{47}$ was performed by placing an aperture in front of the detector. The non-linear refraction data can be obtained from the ratio of the closed aperture transmittance divided by the open aperture transmittance. The peak to valley configuration of the trace indicates that the refractive index change of copolymer is negative, signifying self-defocusing effect of copolymer, P(PH-TZ) shown in Fig. 6.10.
Fig. 6.10: Closed aperture z-scan trace of P(PH-TZ).

The normalized transmittance, $T(z)$ for NLR is given by relation (3)\(^{47}\) (equation (5), given in section 2.2.7). The effective non-linear refractive index ($n_2$), the real parts of $\chi^{(3)}$ ($\text{Re} \chi^{(3)}$) and third-order non-linear susceptibility ($\chi^{(3)}$) of P(PH-TZ) copolymer are calculated by following the equations (4)-(6)\(^{47}\) (equations (6)-(8), given in section 2.2.7). The calculated non-linear optical parameters have been compared with reported values in Table 6.3. Non-linearity originated in the copolymer, P(PH-TZ) is due to strong delocalization of $\pi$-electrons. The polymer investigated here is designed based on the donor–$\pi$–acceptor scheme. As evident from Table 6.3, the copolymer synthesized showed large optical non-linearity than the reported ones.
Table 6.3: Calculated values of non-linear absorption, non-linear refraction and non-linear susceptibility of copolymer, P(PH-TZ).

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>B (m/W)</th>
<th>n_2 (esu)</th>
<th>Re χ^(3) (esu)</th>
<th>Im χ^(3) (esu)</th>
<th>χ^(3) (esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(PH-TZ)</td>
<td>3.75×10^-10</td>
<td>-0.58×10^-10</td>
<td>0.09×10^-10</td>
<td>0.09×10^-10</td>
<td>1.27×10^-11</td>
</tr>
<tr>
<td>P3^a</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P2^b</td>
<td>9.4×10^-11</td>
<td></td>
<td></td>
<td></td>
<td>1.57×10^-12</td>
</tr>
<tr>
<td>TPD-PFE^c</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.7×10^-14</td>
</tr>
<tr>
<td>HMePcd^d</td>
<td>5.7×10^-12</td>
<td>3.6×10^-13</td>
<td>1.9×10^-13</td>
<td>4.07×10^-13</td>
<td></td>
</tr>
</tbody>
</table>

^aReproduced from ref. 48, ^bReproduced from ref. 49, ^cReproduced from ref. 50, ^dReproduced from ref. 51.

6.2.7. Optical limiting property

An optical power limiter is a device which has very high transmission for weak optical signals, but becomes opaque for intense optical signals. The optical power limiting property is mainly due to non-linear absorption property of a molecule. The optical power limiting behaviour of the polymer obtained from the OA z-scan curve is shown in Fig. 6.11.

![Optical limiting curve of P(PH-TZ)](image-url)
The optical limiting threshold will determine the ability of the limiter. The lower the limiting threshold value, the better is the optical limiter. Optical limiting threshold of the copolymer, P(PH-TZ) is obtained to be 0.22 GW/cm².

6.3. Experimental

6.3.1. Materials

Phenothiazine (Aldrich, >98 %), cyanuric chloride (2,4,6-trichloro-1,3,5-triazine, Aldrich, 99 %), 1-bromooctane (Aldrich, 99 %), piperidine (Aldrich, 99 %), sodium bicarbonate (Aldrich, 99.5 %), palladium (II) acetate (Pd(OAc)₂, Aldrich, 99.98 %), triphenyl phosphine (PPh₃, Aldrich, 99 %), potassium phosphate (K₃PO₄, Aldrich, >98%), tetrabutylammonium hexafluorophosphate (Bu₄NPF₆, Aldrich, >99 %), bromine (Merck), diethyl ether (Spectrochem Pvt. Ltd.), magnesium sulphate (anhydrous) (MgSO₄, Spectrochem Pvt. Ltd.), n-butyl lithium (Aldrich, ~1.6M in hexane), 2-isopropano-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Aldrich, 97 %), and potassium hydroxide (Spectrochem Pvt. Ltd.) were used as received. Acetonitrile HPLC grade (CH₃CN, Aldrich), dimethyl acetamide (anhydrous) (DMAc, Spectrochem Pvt. Ltd.), chloroform (CHCl₃, Spectrochem Pvt. Ltd.), dichloromethane (CH₂Cl₂, Spectrochem Pvt. Ltd.), tetrahydrofuran HPLC grade (THF, Spectrochem Pvt. Ltd.), n-hexane (Spectrochem Pvt. Ltd.), acetone (Spectrochem Pvt. Ltd.), dimethyl sulphoxide (DMSO, Spectrochem Pvt. Ltd.) and methanol (anhydrous) (MeOH, Spectrochem Pvt. Ltd.) were dried and distilled when necessary according to the standard procedures.

6.3.2. Computation methods

Theoretical calculations were done using computational methods, which have been described in section 2.3.4.
6.3.3. Chemical procedures

6.3.3.1. 2-((N-piperidine)-4,6-dichloro-s-triazine$^{40}$ (3):

A solution of cyanuric chloride (1) (9.22 g, 0.05 mol) in 30 mL acetone was added with stirring to a cold solution (0±5 °C) of sodium bicarbonate (5.3 g) in 50 mL of distilled water, in a two necked flask. This resulted in the formation of slurry of cyanuric chloride. A solution of piperidine (2) (4.3 mL, 0.05 mol) in 5 mL of acetone was added to the cold slurry of cyanuric chloride. The reaction mixture was stirred for 2 h at 0±5 °C. The white product was filtered, dried and recrystallized from ethanol.

Yield :  80 %
M. P.  :  86 °C.
$^1$H NMR 400MHz, CDCl$_3$) : δ 1.6-1.9 (m, 6H), 3.7-3.9 (m, 4H).

6.3.3.2. 10-Octylphenothiazine$^{41}$ (5):

A mixture of phenothiazine (4) (5 g, 25 mmol), KOH (10.0 g, 250 mmol), and DMSO (100 mL) were placed in a 250 mL two-necked flask. The reaction mixture was stirred for 30 min and octyl bromide (3.8 mL, 22.5 mmol) was added drop wise to the reaction mixture in 20 min, and this mixture was stirred for 24 h at room temperature. The reaction mixture was poured into water, extracted with CH$_2$Cl$_2$, and dried with MgSO$_4$. The resulting liquid was purified by column chromatography using hexane as eluent which gave colourless liquid.

Yield :  93 %
$^1$H NMR 400 MHz, CDCl$_3$) : δ 0.87 (t, J=6.8 Hz, 3H), 1.24-1.43 (m, 10H), 1.77 (m, 2H), 3.80-3.84 (t, J=7.2 Hz, 2H), 6.83-6.91 (m, 4H), 7.11-7.15 (m, 4H).
6.3.3.3. 3,7-Dibromo-10-(octyl)-phenothiazine\(^{41}\) (6):  

10-Octylphenothiazine (5) (7.5 g, 0.024 mol) was dissolved in 50 mL of CH\(_2\)Cl\(_2\), and bromine (8.0 g, 0.05 mol) was injected into the solution using a syringe and stirred for 4 h at room temperature. Dilute aqueous NaOH (20 mL) was added to the reaction mixture and kept for 30 min. The reaction mixture was extracted with CH\(_2\)Cl\(_2\) and brine. The concentrated crude product was purified using column chromatography using hexane as the eluent which gave yellow oil.

Yield : 79 %

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)) : \(\delta\) 0.86 (t, \(J=6.4\) Hz, 3H), 1.14-1.51 (m, 10 H), 1.74 (m, 2H), 3.72 (t, \(J=7.2\) Hz, 2H), 6.66 (d, \(J=8.4\) Hz, 2H), 7.18-7.20 (dd, \(J_1=8\) Hz, \(J_2=2.4\) Hz, 2H), 7.24 (d, \(J=8\) Hz, 2H).

6.3.3.4. 10-octyl-3,7-bis(4,4,5,5-tetramethyldioxaborolan-2-yl)-10Hphenothiazine\(^{41}\) (7):  

To a solution of 3,7-dibromo-10-(octyl)-phenothiazine (6) (2 g, 4.262 mmol) in THF (35 mL) at -78 °C, n-butyl lithium (1.6 M in hexane) (5.59 mL, 8.95 mmol) was added. The reaction mixture was stirred at -78 °C, warmed to 0 °C for 20 min and then cooled again to -78 °C for 20 min. 2-Isopropoxy-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane (1.86 g, 10 mmol) was added to the reaction mixture and warmed to room temperature and stirred for 24 h. The reaction mixture was poured into water and organic layer was extracted with ether and brine. The residue was purified by
several reprecipitation from methanol/acetone mixture to provide the product as a slight yellow solid.

Yield : 51 %
M. P. : 87 °C

$^{1}$H NMR (400 MHz, CDCl$_3$) : $\delta$ 0.78 (t, J=6.3 Hz, 3 H), 1.49-1.71 (m, 34 H), 2.4 (m, 2 H), 3.75 (t, J=7.2 Hz 2 H), 6.71 (m, 2 H), 7.48 (m, 2 H), 7.4 (m, 2H).

6.3.3.5. Synthesis of $P$(PH-TZ)(8):

Suzuki polycondensation reaction was used to synthesize phenothiazine-triazine copolymer, $P$(PH-TZ) (8). Dry THF (20 mL) was added to a flask charged with 10 mol% palladium acetate (0.0036 g, 0.016 mmol) and 20 mol% PPh$_3$ (0.0086 g, 0.032 mmol) and stirred for 30 min. To the reaction mixture of 2-(N-piperidine)-4,6-dichloro-s-triazine (3) (0.038 g, 0.164 mmol) and 10-octyl-3,7-bis(4,4,5,5-tetramethyldioxaborolan-2-yl)-phenothiazine (7) (0.1 g, 0.18 mmol), K$_3$PO$_4$ (2 equ. 0.07 g) was added and stirred at 80-90 °C for 72 hours. Copolymer was precipitated from the reaction mixture by adding large amount of methanol. Repeated purification by soxhlet extraction was performed using methanol and hexane to remove oligomers and dried under reduced pressure. The polymer was obtained as yellowish green powder with 60 % of yield.

$^{1}$H NMR (400 MHz, CDCl$_3$) : $\delta$ 0.65-1.9 (m, 21H), 3.8 (m, 6 H), 6.8-7.5 (m, 6 H).
6.3.4. Instrumentation

Copolymer, P(PH-TZ) was characterized by analytical and spectral methods which have been described in section 2.3.3.

6.3.5. NLO Measurements

NLO properties were determined by methods which have been described in section 2.3.6.

6.4. Conclusions

In conclusion, we have developed a new soluble conjugated copolymer of phenothiazine and triazine via standard Suzuki coupling reaction. Structural characterization was performed by FT-IR, $^1$H NMR and XPS. We have performed a theoretical investigation on the copolymer, P(PH-TZ) using density functional theory calculations at two different energy levels. The band gap obtained by DFT/HSE06 method reveals good agreement with the optical band gap. Compared to the homopolymer, copolymer exhibited decreased band gap value (2.5 eV) and red shifted emission. The third-order non-linear optical parameters were studied using z-scan technique. The z-scan results indicate that the polymer exhibits negative non-linear refractive index and positive non-linear absorption and it is calculated to be $-0.58 \times 10^{-10}$ esu and $3.75 \times 10^{-10}$ m/W, respectively. The copolymer exhibits optical power limiting behaviour at 532 nm wavelength. Hence, the polymer investigated seem to be promising candidate for photonic and optoelectronic applications.
References


Novel Soluble Phenothiazine-Triazine Copolymer: Synthesis and Third-order Non-linear Optical Properties


