Chapter 4

Synthesis and Third-order Non-linear Optical Properties of Low Band Gap 3,4-ethylenedioxythiophene-quinoxaline Copolymers*

Abstract

A series of low band gap 3,4-ethylenedioxythiophene (EDOT) and quinoxaline donor-acceptor (D-A) copolymers were designed and their electronic structure and properties were investigated by employing density functional theory (DFT) in the periodic boundary condition using HSE06 exchange correlation functional and 6-31G basis set. The acceptors investigated were acenaphthylene, phenyl and phenanthrene substituted quinoxaline units. DFT calculations have been performed for both monomers and model oligomers to analyse their electronic properties. The designed copolymers have been synthesized through a simple and facile method, i.e., direct arylation reaction. The photophysical and electrochemical properties of EDOT-quinoxaline copolymers were investigated. The copolymers, P(EDOT-ACEQX), P(EDOT-BZQX), and P(EDOT-PHQX) exhibited theoretical band gap of 1.81, 1.76 and 1.63 eV, respectively using the DFT/HSE06/6-31G calculation and the optical band gap of 1.80, 1.75, and 1.66 eV, respectively, according to the onset edge of lower energy peak of the polymers in solution. Electrochemical studies demonstrated that quinoxaline moieties elevated the HOMO (highest occupied molecular orbital) level and lowered the LUMO (lowest unoccupied molecular orbital) level of the PEDOT (Poly(3,4-ethylenedioxythiophene)) backbone. The theoretical and experimental evaluations revealed the regular alternation of quinoxaline moieties. The band gap of the copolymers was well correlated with the acceptor strength. The experimental results supported the theoretical predictions. The third-order non-linear optical (NLO) properties of D-A EDOT-quinoxaline copolymers, evaluated by z-scan method with nanosecond laser beam at 532 nm, are reported. Polymers possess strong refractive effect with non-linear refraction coefficient of \(-0.47 \times 10^{-10}\), \(-0.95 \times 10^{-10}\) and \(-0.64 \times 10^{-10}\) esu, respectively. Effective third-order non-linear susceptibilities were calculated to be \(0.82 \times 10^{-11}\), \(1.46 \times 10^{-11}\) and \(1.17 \times 10^{-11}\) esu, respectively. Polymers showed good optical limiting behaviour due to two photon absorption (TPA). The results suggest that EDOT-quinoxaline copolymers are promising materials for third-order non-linear optical applications.

4.1. Introduction

Organic conjugated polymers are widely used in electronic devices owing to their good opto-electronic properties. Conjugated polymers with D-A architecture have attracted considerable research interest, since they permit fine tuning of band gap and thereby improved electron or hole affinities. Electronic properties of a polymer can be fine-tuned by structural modification via increasing quinoidal character by alternating electron donor and electron acceptor along the conjugated backbone. Band structure engineering by alternating donor and acceptor groups has become significant in the field of material science, where the mixing of monomer segments with high HOMO and low LUMOs is effective in producing low band gap polymers through efficient inter-chain charge transfer. The D-A copolymers have found a variety of advanced technological applications in the field of light emitting diodes (LEDs), photovoltaic devices, and electrochromic devices, owing to their tunable opto-electronic properties. EDOT based D-A copolymers have been widely studied in several opto-electronic devices, due to strong electron donor effect of ethylenedioxy group. The regular insertion of EDOT unit can serve to raise the HOMO level of the copolymer through self rigidification of conjugated chain by intramolecular sulphur-oxygen interactions. Quinoxaline moieties have proved to be promising acceptors in LEDs, photovoltaic devices and electrochromic devices, owing to their high electron affinity due to the presence of two symmetric unsaturated nitrogen atoms in quinoxaline ring. Here, we have investigated the acceptor strength of quinoxaline units in PEDOT chain by keeping in mind the fact that, both the acceptor strength and the stable geometry govern the optoelectronic properties of D-A copolymers. The
effect of structural changes in the quinoxaline unit on the band gap and energy levels of alternating copolymers of EDOT with acenaphthylene (ACEQX), phenyl (BZQX) and phenanthrene (PHQX) substituted quinoxalines are investigated. In order to get deep insight into the structure-property relationship, the electronic properties were calculated using density functional theory (DFT) adopting two levels of theory. Generally, the quinoxaline copolymers were reported to be synthesized either through Stille,\textsuperscript{22,27,28,33} Suzuki polycondensation\textsuperscript{23-26} or electrochemical reaction,\textsuperscript{29,31,34-37} which make the synthesis tedious and costly. We have attempted to synthesize EDOT-quinoxaline polymers through a simple and facile route, direct arylation reaction.\textsuperscript{38} The results of the investigation of third-order NLO and optical limiting properties of EDOT-quinoxaline copolymers through z-scan technique under nanosecond laser excitation at 532 nm are reported.

4.2. Results and discussion

4.2.1. Electronic structure of model compounds

To investigate the effect of structural change of the quinoxaline derivatives on the band gap of EDOT-quinoxaline copolymers, a sequence of steps were followed involving quantum chemical calculations, based on DFT\textsuperscript{39} at B3LYP\textsuperscript{40-42} and HSE06\textsuperscript{43,44} level of theory using 6-31G basis set. B3LYP/6-31G method was employed to predict the ground state geometries of the model compounds and the relevant electronic structure data of monomers obtained are summarized in Fig. 4.1.
The LUMO levels of ACEQX, BZQX, and PHQX moieties obtained are -1.80, -2.01 and -2.06 eV, respectively. The lower the LUMO energy level, the higher is the acceptor strength. Hence, the quinoxaline acceptor strength follows the order, PHQX > BZQX > ACEQX. As revealed from the energy level diagram, the LUMO level of EDOT-ACEQX, EDOT-BZQX and EDOT-PHQX were calculated to be -2.06, -2.03 and -2.27 eV, respectively, i.e., during coupling, the HOMO levels were elevated and the LUMO levels lowered. The energy gap of the model compounds, EDOT-ACEQX, EDOT-BZQX and EDOT-PHQX followed the order, EDOT-BZQX > EDOT-ACEQX > EDOT-PHQX, which revealed that both the geometry and acceptor strength has played a major role in band gap reduction. This band gap reduction in the D-A monomer is mainly due to the charge transfer between donor, EDOT and acceptor, quinoxaline ring, i.e., the intramolecular charge transfer significantly improves the $\pi$-electron delocalization and thus decreases the bond length alteration (BLA) of EDOT-quinoxaline monomers. This can be visualized from the frontier orbital...
distribution of the model compounds (Fig. 4.2). The wave functions of HOMO and LUMO are localized on the EDOT and quinoxaline unit, respectively.

**Fig. 4.2: Frontier molecular orbital distribution of monomeric units of P(EDOT-ACEQX), P(EDOT-BZQX), and P(EDOT-PHQX) by B3LYP/6-31G method.**

### 4.2.2. Band structure of copolymers

The electronic structure and properties of the copolymers were well studied at the DFT level of theory as implemented in Gaussian 09 software package. In order to account for the reliability of the theoretical results with the experimental results, DFT calculations at two different levels (at B3LYP and HSE06) were carried out. The band structure of the copolymers, P(EDOT-ACEQX), P(EDOT-BZQX) and P(EDOT-PHQX) calculated through HSE06/6-31G level is as shown in Fig. 4.3.
As expected, the regular insertion of quinoxaline unit lowers the LUMO level of PEDOT. From the Fig. 4.3, it could be seen that the band gaps for P(EDOT-ACEQX), P(EDOT-BZQX) and P(EDOT-PHQX) are 1.81, 1.76 and 1.63 eV, respectively, which are in the order of acceptor strength. The band structure data of the copolymers are summarized in Table 4.1. The LUMO level of PEDOT is reduced by a factor of 0.51, 0.61 and 0.82 eV, respectively, by introducing ACEQX, BZQX and PHQX units into the PEDOT backbone. The band gap of P(EDOT-PHQX) is much lower than that of both P(EDOT-BZQX) and P(EDOT-ACEQX).

Table 4.1: Computational data of P(EDOT-ACEQX), P(EDOT-BZQX) and P(EDOT-PHQX) with DFT/B3LYP/6-31G and DFT/HSE06/6-31G methods.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>E_g (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT</td>
<td>-3.62^a</td>
<td>-1.99^a</td>
<td>1.64^c</td>
</tr>
<tr>
<td>P(EDOT-ACEQX)</td>
<td>-4.47^b</td>
<td>-2.20^b</td>
<td>2.27^b</td>
</tr>
<tr>
<td>P(EDOT-BZQX)</td>
<td>-4.31^c</td>
<td>-2.50^c</td>
<td>1.81^c</td>
</tr>
<tr>
<td>P(EDOT-PHQX)</td>
<td>-4.36^b</td>
<td>-2.27^b</td>
<td>2.09^b</td>
</tr>
<tr>
<td></td>
<td>-4.36^c</td>
<td>-2.60^c</td>
<td>1.76^c</td>
</tr>
<tr>
<td></td>
<td>-4.44^c</td>
<td>-2.81^c</td>
<td>1.63^c</td>
</tr>
</tbody>
</table>

^aReproduced from Ref. 47, ^bObtained by the DFT/B3LYP/6-31G method, ^cObtained by the DFT/HSE06/6-31G method.
Significant difference is observed between the values of band gap obtained by the HSE06 and B3LYP methods. The difference between the DFT/B3LYP and HSE06 methods is that HSE06 exchange correlation functional uses an error function screened coulomb potential to calculate the exchange portion of the energy in order to improve computational efficiency.\textsuperscript{43} N. Marom \textit{et al.}, have reported that screened-hybrid functionals such as the HSE approach reduce self-interaction errors in systems possessing both localized and delocalized orbitals and could be applied to both finite and extended systems.\textsuperscript{48}

### 4.2.3. Monomer synthesis

Scheme 1 summarizes the synthesis of key monomers. 2,1,3-Benzo thiadiazole (2) was prepared from o-phenylene diamine (1) and SOCl\textsubscript{2} in DCM. 4,7-Dibromo-2,1,3-benzo thiadiazole (3) was prepared by bromination of 2,1,3-benzo thiadiazole (2) in 47 \% HBr. To obtain 2,3-diamino-1, 4-dibromobenzene (4), 4,7-dibromo-2,1,3-benzo thiadiazole (3) was reduced by NaBH\textsubscript{4} in absolute ethanol. 5,8-Dibromoacenapthylquinoxaline (8), 5, 8-dibromo-2,3-diphenylquinoxaline (9), 10,13-dibromodibenzo[a,c]phenazine (10) were synthesized through condensation reaction of 2,3-diamino-1, 4-dibromobenzene (4) with 1,2-acenaphthaquinone (5), benzil (6) and 9, 10-phenanthrenequinone (7) in ethanol/acetic acid mixture, in 70 \%, 60 \% and 72 \% yields. The compounds were characterized using \textsuperscript{1}H NMR and melting point measurement. All the reactions were performed according to standard procedures.\textsuperscript{49}
Scheme 1: Synthesis of quinoxaline monomers.

4.2.4. Polymer synthesis

The synthetic route toward the EDOT-quinoxaline copolymers is depicted in Scheme 2. The designed copolymers were synthesized by simple and economic method, direct arylation reaction using palladium acetate as catalyst.\textsuperscript{38} It eliminates tedious steps involved in Stille and Suzuki polymerization reactions. The crude polymers were purified by precipitating in methanol followed by Soxhlet extraction using methanol and hexane. The
polymers were soluble in common organic solvents (50 mg/mL) such as chloroform, chlorobenzene and THF. Table 4.2 summarizes the polymerization results including molecular weight, polydispersity index (PDI) and yield of the copolymers. Only low molecular weight polymers were obtained by the polymerization method adopted. The reaction did not proceed to high yield, probably because of the steric hindrance offered by the quinoxaline ring.

Scheme 2: Synthesis of P(EDOT-ACEQX), P(EDOT-BZQX) and P(EDOT-PHQX).
Table 4.2: Results of polymerization reaction.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>PDI</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(EDOT-ACEQX)</td>
<td>3789</td>
<td>6595</td>
<td>1.74</td>
<td>40</td>
</tr>
<tr>
<td>P(EDOT-BZQX)</td>
<td>3207</td>
<td>6300</td>
<td>1.96</td>
<td>45</td>
</tr>
<tr>
<td>P(EDOT-PHQX)</td>
<td>4556</td>
<td>6048</td>
<td>1.90</td>
<td>35</td>
</tr>
</tbody>
</table>

$^a$Determined by GPC in THF based on polystyrene standards.

4.2.5. Structural characterization

The EDOT-quinoxaline copolymers were characterized by FT-IR (Fig. 4.4), $^1$H NMR and XPS. FT-IR spectra of the P(EDOT-ACEQX) showed the following peaks: 3055 cm$^{-1}$ (aromatic C-H stretching), 2949 cm$^{-1}$ (aliphatic C-H stretching of ethylenedioxy group), 1551 cm$^{-1}$ (aromatic C-C and C=N stretching of quinoxaline unit), 1062 cm$^{-1}$ (C-O-C stretching vibration of ethylenedioxy group). The broad band around 1659 cm$^{-1}$ was attributed to the polyconjugation in P(EDOT-ACEQX). Both P(EDOT-BZQX) and P(EDOT-PHQX) had consistent number of peaks as in P(EDOT-ACEQX). The results of FT-IR studies clearly indicated that the copolymerization was successfully achieved.

![Fig. 4.4: FT-IR spectra of (a) P(EDOT-ACEQX), (b) P(EDOT-BZQX) and (c) P(EDOT-PHQX).](image-url)
The $^1$H NMR spectra (Fig. 4.5) of P(EDOT-ACEQX), P(EDOT-BZQX) and P(EDOT-PHQX) showed the resonance signals around 4.5 ppm which corresponded to the protons in ethylenedioxy ring of EDOT moieties in the copolymers. Additionally, P(EDOT-ACEQX), P(EDOT-BZQX) and P(EDOT-PHQX) revealed the multiple peaks at 7.8-8.8, 7.2-7.8 and 7.2-7.8 ppm, respectively which were attributed to aromatic protons of acenaphthylene, phenyl and phenanthrene substituted quinoxaline moieties in the copolymers. All the detected peaks are consistent with the proposed structure.

![Fig. 4.5: $^1$H NMR spectra of (A) P(EDOT-ACEQX), (B) P(EDOT-BZQX) and (C) P(EDOT-PHQX).](image-url)
In order to evaluate the core level composition of the quinoxaline copolymers, XPS investigation was carried out. XPS survey scans of copolymers are depicted in Fig. 4.6. As seen in figure, The C1s signal observed at 283 eV, corresponded to the C-C bonding which was irrespective of the type of hybridization in the polymeric conjugated backbone. The N1s signal of copolymers observed at 396 eV, was mainly due to the nitrogen atoms in the quinoxaline moiety, and indicated the presence of C= N bonding. Moreover, the signals at 531 eV was attributed to the presence of O1s in the copolymers, and refers to the presence of C-O bonding in the copolymers. S2s and S2p core levels have signals at 226 and 163 eV, respectively.\textsuperscript{50} XPS results of copolymers are in agreement with the FT-IR and \textsuperscript{1}H NMR results. However, weak signals at 100 and 150 eV are seen in spectrum ‘c’, due to the presence of Si2p and Si2s which are originated from the silicon substrate.

Fig. 4.6: XPS survey scans of (a) P(EDOT-ACEQX), (b) P(EDOT-BZQX) and (c) P(EDOT-PHQX).

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4.2.6. Optical properties

To probe the spectral response of polymers, UV-Visible spectra were monitored both in THF solution and as thin film. The normalized optical absorption spectra of the three quinoxaline copolymers are depicted in Fig. 4.7. All the three quinoxaline polymers revealed two absorption maxima ($\lambda_{\text{max}}$), the first one in the shorter wavelength ranging from 300-450 nm, owing to $\pi-\pi^*$ transition, whereas the second at the longer wavelength region, which refers to intramolecular charge transfer transitions from the donor, EDOT units to the acceptor, quinoxaline moieties. As shown in the figure, the P(EDOT-ACEQX) showed a broad absorption peak at 507 nm with an onset at 687 nm, whereas the P(EDOT-BZQX) and P(EDOT-PHQX) had peaks at 561 and 575 nm with an onset at 707 and 748 nm, respectively. The absorption maximum of P(EDOT-BZQX) and P(EDOT-PHQX) were red shifted by 54 and 68 nm, respectively compared to that of P(EDOT-ACEQX).

Fig. 4.7: UV-Visible spectra of the copolymers in THF solution (a) P(EDOT-ACEQX) (b) P(EDOT-BZQX), (c) P(EDOT-PHQX) and as thin film (d) P(EDOT-ACEQX), (e) P(EDOT-BZQX), (f) P(EDOT-PHQX). The polymer films were spin coated from CHCl$_3$ solution on to glass substrate.
The band gap of the copolymers, P(EDOT-ACEQX), P(EDOT-BZQX) and P(EDOT-PHQX) were calculated to be 1.80, 1.75 and 1.66 eV, respectively according to the onset edge of the lower energy peak of polymer in solution. As expected, the optical band gap varies as the function of the acceptor strength of the quinoxaline units. This could be because ‘greater the acceptor strength of the quinoxaline, greater will be the donor-acceptor interaction’, which leads to greater reduction in the band gap.\textsuperscript{45} Thus, the reduction in the band gap is mainly due to the charge transfer from EDOT unit to the quinoxaline unit. These $E_g^{opt}$ values could be correlated with the theoretical prediction that is obtained by HSE06/6-31G than the B3LYP/6-31G method. Despite the agreement, some deviations still exist due to the negligence of solid state effects such as polarization effects and intermolecular packing forces in the periodic boundary condition calculation.\textsuperscript{51}

The thin film of polymers showed more broad absorption spectra than in solution phase. The $\lambda_{\text{max}}$ of P(EDOT-BZQX) film was red shifted by 21 nm from the corresponding polymer in solution phase. While considering the P(EDOT-ACEQX) and P(EDOT-PHQX), the $\lambda_{\text{max}}$ values are quite similar. The onset of absorption of P(EDOT-ACEQX), P(EDOT-BZQX) and P(EDOT-PHQX) were red shifted by 37, 103, and 34 nm, respectively. The band gap of P(EDOT-ACEQX), P(EDOT-BZQX), and P(EDOT-PHQX) obtained are 1.71, 1.53, and 1.58 eV, respectively. The significant redshift in band gap suggests reduction in conformational freedom, less solvent interaction, and aggregation/ordered arrangement in the solid state. Here, the band gap did not vary systematically with acceptor strength of quinoxaline unit. This could be due to the influence of polymer geometry. The geometry of the donor-acceptor material was significantly affected by
the ring size and intramolecular charge transfer;\textsuperscript{45} i.e., the lower band gap of P(EDOT-BZQX) could be attributed to the structural planarity compared to the P(EDOT-ACEQX) and P(EDOT-PHQX), owing to the π-π interaction between the polymer chains.

4.2.7. Electrochemical studies

The electrochemical behaviour of the copolymers was investigated by cyclic voltammetry (CV). Electrochemical methods provide a means of establishing the HOMO and LUMO energies of conjugated polymers. The redox behaviour of polymer was measured using polymer coated platinum (Pt) electrode as working electrode, Pt wire as the counter, and Ag/Ag\textsuperscript{+} as the reference electrodes in 0.1 M Bu\textsubscript{4}NPF\textsubscript{6}-acetonitrile solution. The electrochemical data of the polymers are summarized in Table 4.3. The HOMO and LUMO were estimated from the onset of oxidation and reduction potential according to the equation proposed by Bredas.\textsuperscript{52}

The HOMO levels of P(EDOT-ACEQX), P(EDOT-BZQX) and P(EDOT-PHQX) are obtained to be -2.72, -2.65, and -2.66 eV, respectively. The LUMO levels were calculated to be -3.77, -3.65, and -3.65 eV, for P(EDOT-ACEQX), P(EDOT-BZQX) and P(EDOT-PHQX), respectively. The band gap of the copolymers were calculated to be 1.05, 1.0, and 0.99 eV, respectively, for P(EDOT-ACEQX), P(EDOT-BZQX) and P(EDOT-PHQX). The band gap of copolymers followed the order, P(EDOT-ACEQX) > P(EDOT-BZQX) > P(EDOT-PHQX), in the order of acceptor strength. The copolymers have relatively low LUMO energy compared to PEDOT, indicating better electron accepting/transporting property.\textsuperscript{51} The electrochemical band gap showed deviations of the order of 0.6-0.75 eV.
from the optical band gap. This could be due to the difference in the mechanism of optical excitation and electrochemical oxidation/reduction processes. In the former process, excitation creates excitons (bound electrons and hole pair) and the latter process creates ions. The low energy of excitons, compared to the ions and solvation of the ions during electrochemical experiment was reflected in the observed electrochemical band gap.

Table 4.3: Electrochemical data of P(EDOT), P(EDOT-ACEQX), P(EDOT-BZQX), P(EDOT-PHQX), P(EDOT-ACEQX-EDOT) and P(EDOT-BZQX-EDOT).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Onset oxdn (V)</th>
<th>HOMO (eV)</th>
<th>Onset Redn(V)</th>
<th>LUMO (eV)</th>
<th>Eg (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(EDOT)()(^a)</td>
<td>-3.62</td>
<td>-1.99</td>
<td></td>
<td>1.64</td>
<td></td>
</tr>
<tr>
<td>P(EDOT-ACEQX)(^b)</td>
<td>-1.68</td>
<td>-2.72</td>
<td>-0.63</td>
<td>-3.77</td>
<td>1.05</td>
</tr>
<tr>
<td>P(EDOT-BZQX)(^b)</td>
<td>-1.75</td>
<td>-2.65</td>
<td>-0.75</td>
<td>-3.65</td>
<td>1.0</td>
</tr>
<tr>
<td>P(EDOT-PHQX)(^b)</td>
<td>-1.74</td>
<td>-2.66</td>
<td>-0.75</td>
<td>-3.65</td>
<td>0.99</td>
</tr>
<tr>
<td>P(EDOT-ACEQX-EDOT)(^c)</td>
<td>-1.14</td>
<td>-0.51</td>
<td></td>
<td>0.93</td>
<td></td>
</tr>
<tr>
<td>P(EDOT-BZQX-EDOT)(^d)</td>
<td></td>
<td></td>
<td></td>
<td>1.01</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Reproduced from Ref. 45, \(^b\)Determined by CV, \(^c\)Reproduced from Ref. 35, \(^d\)Reproduced from Ref. 37.

4.2.8. Photoluminescence (PL) properties

The PL emission spectra of copolymers in THF and as film are shown in Fig. 4.8. In solution, copolymers exhibited distinct emission at 653, 672 and 731 nm for P(EDOT-ACEQX), P(EDOT-BZQX) and P(EDOT-PHQX), respectively. The red shift in emission maximum is observed for P(EDOT-BZQX) and P(EDOT-PHQX) compared to that of P(EDOT-ACEQX). The polymers exhibited emission max in the order of P(EDOT-PHQX) > P(EDOT-BZQX) > P(EDOT-ACEQX), which are in the order of acceptor strength of quinoxaline units.
To get insight into the intramolecular charge transfer process, PL spectra of thin films have been investigated. In thin film, all the copolymers revealed broad and red shifted emission with a tail extending to lower energy side of the spectrum, which indicated the efficient intramolecular charge transfer in copolymers. The emission peaks of P(EDOT-ACEQX), P(EDOT-BZQX) and P(EDOT-PHQX) in thin films are red shifted to around 692, 803 and 740 nm, respectively. This can be attributed to the reduced torsion angles between the adjacent units and hence the energy levels are affected in various degrees. In thin film, polymers exhibited emission maximum in the order of P(EDOT-BZQX) > P(EDOT-PHQX) > P(EDOT-ACEQX). The red shift of emission of these alternating copolymers is not in consistence with the increasing order of acceptor strength of quinoxaline units. The variation in emission maximum of P(EDOT-BZQX) could be due to better delocalization and thus better intramolecular charge transition.
The most reliable method for determining the quantum yield is the comparative method proposed by Williams et al., which involve the use of well-known studied samples with known quantum yield ($\Phi$) values. The absolute PL quantum yield of the polymers in solution was estimated by plotting the magnitude of the integrated fluorescence intensity against solution absorbance. Absolute values were calculated using the standard sample, rhodamine 6G ($\Phi_{std} = 0.75$ in chloroform), according to the following equation (1),

$$\phi_p = \frac{Grad_p \times \phi_{std}}{Grad_{std}}$$ ......................................................... (1)

where, the subscripts ‘p’ and ‘std’ denote polymer and standard, respectively and ‘Grad’ is the gradient from the plot of integrated fluorescence intensity vs. absorbance. The quantum yield of P(EDOT-ACEQX), P(EDOT-BZQX) and P(EDOT-PHQX), was obtained to be 0.21, 0.20 and 0.29, respectively. No systematic variation in the PL quantum yield with acceptor strength of quinoxaline units was observed.

**4.2.9. Thermal properties**

The thermal stability of the copolymers was investigated by both TGA and DSC. The TG traces of copolymers are depicted in Fig. 4.9. As shown in the figure, the copolymers reveal step wise degradation. DSC is devoid of any characteristic peak in the temperature range of 40 and 200 °C. This confirms the suitability in device applications. On the basis of TGA exotherm, the thermal decomposition temperature for P(EDOT-ACEQX), P(EDOT-BZQX) and P(EDOT-PHQX) were determined to be 146, 328 and 140 °C, respectively, choosing 5% weight loss at the onset loss point. The
P(EDOT-ACEQX) copolymer showed the degradation temperature at 173, 402 and 440°C. While P(EDOT-BZQX) showed the degradation temperature of 406 and 435 °C. Whereas the copolymer P(EDOT-PHQX) showed the significant weight losses at 170, 250, 390 and 440 °C. The lower thermal stability of quinoxaline copolymers could be attributed to the presence of azomethine bonds which are highly prone to degradation. The copolymer, P(EDOT-BZQX) displayed more thermal stability than P(EDOT-ACEQX) and P(EDOT-PHQX), owing to the lack of ring strain in phenyl substituted quinoxaline when compared to the others.

![Fig. 4.9: TG traces of polymers (a) P(EDOT-ACEQX), (b) P(EDOT-BZQX) and (c) P(EDOT-PHQX).](image)

**4.2.10. Non-linear optical properties**

The third-order NLO parameters of EDOT-quinoxaline copolymers were investigated using z-scan technique. To study the non-linear optical absorption of polymers, the open aperture (OA) z-scan technique was conducted at 532 nm. The OA trace of quinoxaline copolymers in dilute CHCl₃ (A) and as thin film (B) is shown in Fig. 4.10.
Fig. 4.10: Open aperture z-scan traces of (a) P(EDOT-ACEQX), (b) P(EDOT-BZQX) and (c) P(EDOT-PHQX), in solution (A) and as film (B) at 112 μJ.

In solution phase, copolymers depict a normalized transmittance valley, indicating the reverse saturation (RSA) type of absorption with a positive NLO absorption coefficient. However, the z-scan data of copolymer film show enhanced transmittance at the focus, indicating saturation absorption (SA) type behaviour with a negative NLO absorption coefficient. The switch over from RSA to SA could be attributed to ground state band bleaching of polymers in film phase. The normalized transmittance for the standard OA z-scan is expressed by the equation (2) (equation (3), given in section 2.2.7.). The theoretical curves obtained with the equation (2) (equation (3), given in section 2.2.7.) were fitted with the experimental data for SA and RSA and the effective non-linear absorption coefficients, $\beta$ for the copolymers were calculated. Also the imaginary part of the third-order susceptibility (Im $\chi^{(3)}$) of copolymers is determined by equation (3) (equation (4), given in section 2.2.7.).

Closed aperture (CA) z-scan measurements with aperture in front of the detector were performed to study the non-linear refractive index of the
polymers in CHCl$_3$. Fig. 4.11 shows the CA traces of EDOT-quinoxaline copolymers in CHCl$_3$. The CA traces show the transmittance maximum (peak) followed by transmittance minimum (valley) pattern for all the solutions. Thus, all the copolymers exhibited strong self-defocusing behaviour and negative non-linear refraction coefficient, $n_2$ as revealed in the peak-valley patterns. Since the CA transmittance is affected by both non-linear refraction and non-linear absorption, it is necessary to eliminate the effect of non-linear absorption from that of non-linear refraction. This could be achieved by dividing the CA z-scan data by the corresponding OA data. The normalized transmittance, $T(z)$ for non-linear refraction$^{57}$ is given by the relation (4) (equation (5), given in section 2.2.7.). The non-linear refractive index ($n_2$), the real parts of $\chi^{(3)}$ (Re $\chi^{(3)}$) and third-order non-linear susceptibility ($\chi^{(3)}$) of EDOT-quinoxaline copolymers is calculated by the following equations (5)-(7)$^{57}$ (equations (6)-(8), given in section 2.2.7.).

Fig. 4.11: Closed aperture z-scan traces of (A) P(EDOT-ACEQX), (B) P(EDOT-BZQX) and (C) P(EDOT-PHQX) at 112 $\mu$J.

The calculated values of non-linear absorption coefficient ($\beta$, m/W), the non-linear refraction coefficient ($n_2$, esu) and the third-order non-linear susceptibility ($\chi^{(3)}$, esu) at 112 $\mu$J are given in Table 4.4. The $\beta$ value of P(EDOT-ACEQX), P(EDOT-BZQX) and P(EDOT-PHQX) is obtained to
be $1.58 \times 10^{-10}$, $0.4 \times 10^{-10}$ and $2.54 \times 10^{-10}$ m/W, respectively. Furthermore, the $\chi^{(3)}$ value is found to be $0.82 \times 10^{-11}$, $1.46 \times 10^{-11}$ and $1.17 \times 10^{-11}$ esu, respectively. Copolymers show strong optical non-linearity, due to donor-acceptor scheme. Here, non-linearity is mainly due to the charge transfer from donor to acceptor unit, i.e., due to strong delocalization of $\pi$ electrons. The results also indicate that the structure of the copolymers have great impact on NLO properties. In film, saturation intensity ($I_s$) was calculated using the equation $I_s = -\alpha_o/2\beta$ and it was found to be $1.3 \times 10^5$, $1.6 \times 10^5$ and $1.47 \times 10^5$ W/m$^2$ for P(EDOT-ACEQX), P(EDOT-BZQX) and P(EDOT-PHQX), respectively, that too not in the order of acceptor strength.

**Table 4.4: Values of non-linear absorption, non-linear refraction, and non-linear susceptibility of P(EDOT-ACEQX), P(EDOT-BZQX) and P(EDOT-PHQX) at 112 $\mu$J intensity.**

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Non-linear absorption coefficient ($\beta$, m/W)</th>
<th>Non-linear refractive index ($n_2$, esu)</th>
<th>Imaginary part of non-linear susceptibility ($\text{Im} \chi^{(3)}$, esu)</th>
<th>Real part of non-linear susceptibility ($\text{Re} \chi^{(3)}$, esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(EDOT-ACEQX)</td>
<td>$1.58 \times 10^{-10}$</td>
<td>$-0.47 \times 10^{-10}$</td>
<td>$0.04 \times 10^{-10}$</td>
<td>$-0.72 \times 10^{-11}$</td>
</tr>
<tr>
<td>P(EDOT-BZQX)</td>
<td>$2.4 \times 10^{-10}$</td>
<td>$-0.95 \times 10^{-10}$</td>
<td>$0.01 \times 10^{-10}$</td>
<td>$-1.42 \times 10^{-11}$</td>
</tr>
<tr>
<td>P(EDOT-PHQX)</td>
<td>$2.54 \times 10^{-10}$</td>
<td>$-0.64 \times 10^{-10}$</td>
<td>$0.06 \times 10^{-10}$</td>
<td>$-1.0 \times 10^{-11}$</td>
</tr>
<tr>
<td>P3</td>
<td>$1.57 \times 10^{-12}$</td>
<td></td>
<td></td>
<td>$1.57 \times 10^{-12}$</td>
</tr>
<tr>
<td>P2</td>
<td>$9.4 \times 10^{-11}$</td>
<td></td>
<td></td>
<td>$2.7 \times 10^{-11}$</td>
</tr>
<tr>
<td>TPD-PFE</td>
<td>$5.7 \times 10^{-14}$</td>
<td></td>
<td></td>
<td>$5.7 \times 10^{-14}$</td>
</tr>
<tr>
<td>P</td>
<td>$3.0 \times 10^{-11}$</td>
<td></td>
<td></td>
<td>$6.25 \times 10^{-12}$</td>
</tr>
<tr>
<td>P1</td>
<td>$1.3 \times 10^{-11}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HMePc</td>
<td>$5.7 \times 10^{-12}$</td>
<td>$3.6 \times 10^{-13}$</td>
<td>$1.9 \times 10^{-13}$</td>
<td>$4.07 \times 10^{-13}$</td>
</tr>
</tbody>
</table>

*Reproduced from ref. 58, Reproduced from ref. 59, Reproduced from ref. 60, Reproduced from ref. 61, Reproduced from ref. 62, Reproduced from ref. 63.

The results revealed that the copolymers investigated in the present study have a good non-linear optical response and are comparable to or even
better than the D-A copolymers reported in the literature (given in Table 4.4), and hence could be chosen as ideal candidates with potential applications for non-linear optics.

Fig. 4.12: The open-aperture z-scan traces of (A) P(EDOT-ACEQX), (B) P(EDOT-BZQX) and (C) P(EDOT-PHQX) at (a) 55, (b) 112 and (c) 141 μJ input fluences.

Fig. 4.12 shows variation of non-linear transmission of copolymers at different input fluences (55, 112 and 141 μJ). The calculated values of \( \beta \) at different fluences are gathered in Table 4.5. From the results it is clear that there is considerable variation in the non-linear absorption with input fluences.

Table 4.5: Calculated values of non-linear absorption coefficient of P(EDOT-ACEQX), P(EDOT-BZQX) and P(EDOT-PHQX) at 55, 112 and 141 μJ intensity.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( \beta ) (m/W) at 55 μJ</th>
<th>( \beta ) (m/W) at 112 μJ</th>
<th>( \beta ) (m/W) at 141 μJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(EDOT-ACEQX)</td>
<td>( 1.38 \times 10^{-10} )</td>
<td>( 1.58 \times 10^{-10} )</td>
<td>( 2.12 \times 10^{-10} )</td>
</tr>
<tr>
<td>P(EDOT-BZQX)</td>
<td>( 0.62 \times 10^{-10} )</td>
<td>( 2.4 \times 10^{-10} )</td>
<td>( 3.6 \times 10^{-10} )</td>
</tr>
<tr>
<td>P(EDOT-PHQX)</td>
<td>( 1.76 \times 10^{-10} )</td>
<td>( 2.54 \times 10^{-10} )</td>
<td>( 5.27 \times 10^{-10} )</td>
</tr>
</tbody>
</table>
4.2.11. Optical power limiting

To investigate the optical limiting property of the polymers, the non-linear transmission is measured as a function of input fluence. A material which transmits light at low input intensities and become opaque at high inputs is called optical limiter. Optical limiting property of a material is mainly due to absorptive non-linearity, which corresponds to the imaginary part of third-order susceptibility, i.e., it could be due to TPA, free carrier absorption, RSA, self-focusing, self-defocusing or induced scattering. Thus, the optical limiting property of EDOT-quinoxaline copolymers was studied by a standard OA z-scan technique at 532 nm. As shown in Fig. 4.13, the approximate fluence at which the normalized transmission begins to deviate from linearity corresponds to optical limiting threshold and it is found to be 0.41, 0.35 and 0.41 GW/cm² for P(EDOT-ACEQX), P(EDOT-BZQX) and P(EDOT-PHQX), respectively, which are not in the order of acceptor strength of quinoxaline unit. In conjugated polymeric materials, electrons can move in the molecular orbitals, which results from the linear superposition of the carbon π atomic orbitals. This leads to high optical non-linearity, which increases with conjugation length. On the other hand, non-linearity is the result of an optimum combination of various factors such as π-delocalization length, donor-acceptor groups, dimensionality, conformation, and orientation for a given molecular structure. The results indicate that these polymers can be used for optical power limiting at high laser fluences.
4.3. Materials and methods

4.3.1. Materials

3,4-Ethlenedioxythiophene (EDOT, Aldrich, 98 %), o-phenylene diamine (Merck, 98 %), tetrabutyl ammonium bromide (TBAB, Avra synthesis Pvt. Ltd., 98 %), sodium acetate (anhydrous) (Spectrochem Pvt. Ltd.), triethyl amine (Spectrochem Pvt. Ltd.), palladium (II) acetate (Aldrich, 99.98 %), tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$, Aldrich, >99 %), thionyl chloride (SOCl$_2$, Merck, 97 %), hydrobromic acid (HBr, Spectrochem Pvt. Ltd., 47 %), bromine (Merck), sodium borohydride (NaBH$_4$, Merck, 98%), ethanol absolute (Merck), diethyl ether (Spectrochem Pvt. Ltd.), magnesium sulphate (anhydrous) (MgSO$_4$, Spectrochem Pvt. Ltd.), acenaphthenequinone (Aldrich), benzil (Aldrich, 98 %), phenanthrene-9,10-dione (Aldrich, 95 %) and glacial acetic acid were used as received. Acetonitrile HPLC grade (CH$_3$CN, 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.), hexane (Spectrochem Pvt. Ltd.) and methanol (anhydrous) (MeOH, Spectrochem Pvt. Ltd.) were dried and distilled when necessary according to the standard procedures.

4.3.2. Computation methods

Theoretical calculations were done using computational methods, which has been described in section 2.3.4.

4.3.3. Chemical procedures

4.3.3.1. Synthesis of 5,8-dibromoacenaphthyl quinoxaline (ACEQX) (8):

A solution of 2,3-diamino-1,4-dibromobenzene (4) (0.15 g, 0.56 mmol) (section 3.3.3.3) and acenaphthenequinone (5) (0.10 g, 0.55 mmol) in ethanol (20 mL) and few drops of glacial acetic acid was heated to reflux for 1h, and cooled to 0 °C. The precipitate formed was separated by filtration and washed with ethanol to afford 5,8-dibromoacenaphthyl quinoxaline (8) as light yellow solid.

Yield : 70 %

¹H NMR (400 MHz, CDCl₃) : δ 8.54 (d, 2H), 8.15 (d, 2H), 7.92 (s, 2H), 7.89-7.86 (m, 2H).

4.3.3.2. Synthesis of 5,8-dibromo-2,3-diphenyl quinoxaline (BZQX) (9):

A solution of 2,3-diamino-1,4-dibromobenzene (4) (1.0 g, 3.8 mmol) (section 3.3.3.3) and benzil (6) (0.80 g, 3.8 mmol) in ethanol (40 mL) and few drops of glacial acetic acid was heated to reflux for 1h, and cooled to
0 °C. The precipitate formed was isolated by filtration and washed with ethanol to afford 5,8-dibromo-2,3-diphenyl quinoxaline (9) as light yellow solid.

<table>
<thead>
<tr>
<th>Yield</th>
<th>60 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>M. P.</td>
<td>221 °C</td>
</tr>
</tbody>
</table>

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.92 (s, 2H), 7.64 (m, 4H), 7.37 (m, 6 H).

4.3.3.3. **Synthesis of 10,13-dibromodibenzo[a,c]phenazine (PHQX) (10):**

A solution of 2,3-diamino-1,4-dibromobenzene (4) (1.03 g, 3.9 mmol) (section 3.3.3.3) and phenanthrene-9,10-dione (7) (0.81 g, 3.9 mmol) in 42 mL ethanol/acetic acid (20:1) was heated to reflux for 2 h, and cooled to 0 °C. The precipitate formed was isolated by filtration and washed with ethanol to afford 10,13-dibromodibenzo[a,c]phenazine (10) as yellow solid.

<table>
<thead>
<tr>
<th>Yield</th>
<th>72 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>M. P.</td>
<td>317 °C</td>
</tr>
</tbody>
</table>

$^1$H NMR (400 MHz, CDCl$_3$): δ 9.48 (dd, J1=8 Hz, J2=1.2 Hz, 2 H), 8.57 (dd, J1=8 Hz, J2=0.8 Hz, 2 H), 8.04 (s, 2H), 7.87-7.83 (dt, J1=15.2 Hz, J2=1.6 Hz, 2 H), 7.81-7.77 (dt, J1=13.2 Hz, J2=1.2 Hz, 2 H).

4.3.3.4. **Synthesis of P(EDOT-ACEQX) (12):**

To a stirred solution of EDOT (11) (0.024 g, 0.17 mmol) in 10 mL DMAc was added TBAB (0.05 g, 0.17 mmol) and sodium acetate (0.05 g, 0.68 mmol). The reaction mixture was stirred at room temperature for 30 min followed by addition of 5,8-dibromoacenaphthyl quinoxaline (8)
Chapter 4

(0.07 g, 0.17 mmol) and 10 % palladium acetate (0.003 g). The reaction mixture was stirred at 90 °C for 48 h. The reaction mixture was cooled to room temperature and poured in to methanol (20 mL). The precipitate was filtered and washed with methanol. The polymer was purified by soxhlet extraction using hexane and methanol for 24 h. The residue was dissolved in minimum amount of CHCl₃ and precipitated using methanol and dried under vacuum.

Yield : 40%

FT-IR (νmax/cm⁻¹) : 3055br (C-H ar), 2949s (C-H),
1551w (C-C/C=N), 1062s and
905w (C-O), 1659br (conjugation).

¹H NMR (400 MHz, d8-THF) : δ (ppm): 4.3 (m, 2H), 4.5 (m, 2H),
7.6 (s, 1H), 7.8 (m, 2H), 8.1 (m, 2H),
8.4 (m, 2H), 8.7 (m, 2H).

4.3.3.5. Synthesis of P(EDOT-BZQX) (13):

To a stirred solution of EDOT (11) (0.024 g, 0.17 mmol) in 10 mL DMAc was added TBAB (0.05 g, 0.17 mmol) and sodium acetate (0.05 g, 0.68 mmol). The reaction mixture was stirred at room temperature for 30 min followed by addition of 5,8-dibromo-2,3-diphenylquinoxaline (9) (0.074 g, 0.17 mmol) and 10% palladium acetate (0.003 g). The reaction mixture was stirred at 90 °C for 48 h. The reaction mixture was cooled to room temperature and poured in to methanol. The precipitate was filtered and washed with methanol. The polymer was purified by soxhlet extraction using hexane and methanol for 24 h. The residue was dissolved in minimum amount of CHCl₃ and precipitated using methanol and dried under vacuum.
Yield : 45 %.
FT-IR ($\nu_{\text{max}}$/cm$^{-1}$): 3055br (C-H ar), 2951s (C-H),
1567w (C-C/C=N), 1062s and 905w (C-O), 1651br (conjugation).

$^1$H NMR (400 MHz, d8-THF): $\delta$ (ppm): 4.5 (m, 4H), 6.9 (s, 1H), 7.0 (m, 2H), 7.4 (m, 2H), 7.6 (m, 2H), 8.7 (m, 2H).

4.3.3.6. Synthesis of P(EDOT-PHQX) (14):

To a stirred solution of EDOT (11) (0.024 g, 0.17 mmol) in 10 mL DMAc was added TBAB (0.05 g, 0.17 mmol) and sodium acetate (0.05 g, 0.68 mmol). The reaction mixture was stirred at room temperature for 30 min followed by addition of 10,13-dibromodibenzo[a,c]phenazine (10) (0.074 g, 0.17 mmol) and 10% palladium acetate (0.003 g). The reaction mixture was stirred at 90 °C for 48 h. The reaction mixture was cooled to room temperature and poured in to methanol. The precipitate was filtered and washed with methanol (20 mL). The polymer was purified by soxhlet extraction using hexane and methanol for 24 h. The residue was dissolved in minimum amount of CHCl$_3$ and precipitated using methanol and dried under vacuum.

Yield : 35 %.
FT-IR ($\nu_{\text{max}}$/cm$^{-1}$): 3052br (C-H ar), 2956s (C-H),
1537w (C-C/C=N), 1062s and 905w (C-O), 1636br (conjugation).

$^1$H NMR (400 MHz, d8-THF): $\delta$ (ppm): 4.7 (m, 4H), 6.9 (s, 1H), 7.1 (m, 2H), 7.6 (m, 2H), 7.7 (m, 2H), 7.8 (m, 2H).
4.3.4. Instrumentation

EDOT-quinoxaline copolymers were characterized by instrumentation methods which have been described in section 2.3.3.

4.3.5. NLO Measurements

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

4.4. Conclusions

Three alternating D-A EDOT-quinoxaline copolymers were designed and have been synthesized by an economic method, direct arylation from the corresponding EDOT and quinoxaline monomers. The electronic structure of copolymers were calculated using HSE06/6-31G and B3LYP/6-31G method. Theoretically predicted values are in good agreement with the optical band gap. The copolymers, P(EDOT-ACEQX), P(EDOT-BZQX), and P(EDOT-PHQX) exhibited electrochemical band gap of 1.05, 1.0 and 0.99 eV, respectively. The reduction in band gap is the function of the acceptor strength of the quinoxaline unit. Third-order non-linear optical parameters of EDOT-quinoxaline copolymers were studied by z-scan technique. The z-scan results imply that the copolymers exhibited negative non-linear absorption and the $\beta$ value was obtained to in the order of $10^{-10}$ m/W. The non-linear refractive index of copolymers was found to be negative and it was in the order of $10^{-11}$ esu.
References


Chapter 4


Chapter 4


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