Investigation of the Electronic and pH-Sensing properties of Hydroxyl-Functionalized Imine-Linked Polymers via the UV-Vis Absorption Spectra and the Density Functional Theory (DFT) Calculations

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ABSTRACT

In this report, a synergetic computational and experimental studies were demonstrated on examples of poly-imine polymers; P(PI-IPI) and P(PIOH-IPI) to explore the role of hydroxyl substituent on their sensing and electronic properties. The polymer P(PIOH-IPI) bearing the OH-group on the ortho-position to the imine-bond, while the structure of the polymer P(PI-IPI) reveal the imine-bond only. The sensing property of the polymers was investigated via the UV-vis absorption in different solvents, acidic and basic solutions. Both polymers have shown significant sensing behavior in the acidic medium, while unpronounced behavior was noticed in the case of the polymer P(PI-IPI) in basic medium. Upon the incorporation of the OH-group, the polymer P(PIOH-IPI) has indistinguishable sensing behavior, a similar blue-shift in the acidic and basic medium, which can be attributed to the presence and the position of OH-group. The optical band gap of the polymers was determined experimentally and theoretically from the UV-vis absorption spectra and DFT calculations in the DMSO solvent. Other factors that affect the band gap values such as the structural conformation and length of conjugation were explored theoretically. In general, as the length of the optimized chain increased, the spectrum is red-shifted and the band gap decreased, which is attributed to the possible loss of chain planarity and conjugation beyond the monomer structure. Interestingly, the UV-vis spectra of the monomer-optimized structures were in a good match with the experimental UV-vis spectra. However, the band gap difference can be attributed to the method of band gap determination.

Key word: Sensing, Functionalization, conformation, Length of conjugation, DFT, UV-vis

INTRODUCTION

Imine-linked polymers (ILPs) are organic conjugated polymers that gained significant importance due to their vital applications in the fields of catalysis, sensing, gas sorption, electronic and optoelectronic devices, sensors and other more applications [1-7]. The multifunctional properties of ILPs are related to their selective structural design which, exhibit an extended conjugated backbone accessible for functionalization and free nitrogen sites available for protonation and metal ion-coordination [3, 8, 9].

As example, ILPs-based polymers such as C3v-POF and Th-POF were synthesized as Cu- and Ir- coordinated polymers and used as catalysts in the hydrogenation and cyclopropanation reactions, while other ILPs were used as Suzuki coupling catalysts [9-11].
In the field of environmental science, ILP-1 and PPFs are porous ILPs performed well as candidates for gas sorption and separation applications [12]. Furthermore, the usefulness of ILPs was evaluated in the laboratories as sensors for explosive nitro-aromatic compounds and to distinguish solutions at different pH’s [13-15]. ILPs were also used as template for tailoring the electronic properties via controlling the size and shape of semiconducting ZnO nanoparticles [16, 17]. Recently, we have reported new series of functionalized ILPs as promising materials for optoelectronics devices fabrications, due to the changes in their electronic properties upon functionalization [18]. However, we have concluded, as also found by others, that the type of the introduced functional group will direct the material for specific applications and may not reach the target in some cases.

Accordingly, in this manner, we have systematically expanded our pervious study and controlled the factors of the backbone chain contents, the type, and position of the substituent. In specific, we have synthesized two ILPs exhibit similar structural components, while one of them functionalized with electron-donating (OH-group). The effect of the OH-substituent was studied by others on small Schiff bases molecules via the experimental and computational calculations. Thus, and motivated by others, we have investigated the impact of the OH-group on the pH-sensing and the electronic properties (e.g. the optical band gap) of the polymers by using UV-vis absorption measurements and density functional theory calculations (DFT). The DFT calculations were performed for comparison purposes between the experimentally measured and calculated UV-vis spectra and to explore the impact of conformation and length of conjugation on the optical band gap.

EXPERIMENT

Chemicals and instrumentation

All chemicals and solvents were purchased from Sigma-Aldrich and used without further purification, unless otherwise noted. 2,5-Diaminohydroquinone dihydrochloride, Benzenediamine and terephthaldehyde were purchased from sigma Aldrich. IR spectra were recorded on a Shimadzu FT-IR-8300 on KBr pellets in the wavenumber range 400-4000 cm\(^{-1}\). UV-Vis measurements were carried out using Shimadzu UV spectrometer UV-1800. Thermogravimetric analysis (TGA) were carried out using TA Instruments Q-5000IR series thermal gravimetric analyzer with samples held in 50 μL platinum pans under the nitrogen atmosphere (heating rate 10 °C/min ). The elemental analysis of carbon, nitrogen, hydrogen and sulfur analyses were performed using a Vario EL elemental analyzer.

Procedure reaction/ Synthesis of Polymers

The polymers are synthesized as reported in the previous literature [18-20]. An equimolar of terephthalaldehyde (Tph-CHO) and aryl-diamines was mixed in acetonitrile solution at RT and stirred for 6 hr. The resulted brown suspension was filtered, washed with HCl (0.1 M), NaOH (0.1 M), and acetone (20 mL) and dried. The percent yields and spectrochemical characterizations are reported below.

Synthesis of P(PI-IPI)

The synthesis of poly(phenyl-azomethine-phenyl) P(PI-IPI) was demonstrated by mixing terephthalaldehyde (Tph-CHO), (40 mg, 0.29 mmol) and benzenediamine (DAB), (32.3 mg, 0.29 mmol) and adding HCl (1.0 mL, 0.5 M). The brown solid resulted in good yield (78%). Anal. Calcd (%) for C\(_{14}\)H\(_{10}\)N\(_{2}\): C, 81.53%; H, 4.89%; N, 13.58% Found: C, 80.56%; H, 4.95%; N, 14.33%.
Synthesis of P(PI(OH)-IPI)

The synthesis of poly(2,5-dihydroxybenzene-azomethine-phenyl-azomethine) P(PI(OH)-IPI) was demonstrated by mixing (Tph-CHO), (40 mg, 0.29 mmol), and 2,5-Diaminohydroquinone dihydrochloride (DAH), (52.7 mg, 0.29 mmol). The brown solid resulted in good yield (76%). Anal. Calcd (%) for C_{14}H_{10}N_{2}O_{2}.2H_{2}O: C, 70.58%; H, 4.23%; N, 11.76%; O, 13.43% Found: C, 60.99%; H, 5.12%; N, 10.33%; O, 23.56%.

RESULT AND DISCUSSION
Synthesis and Characterization and Physiochemical Properties

The polymers in this study: poly(phenyl-azomethine-phenyl) P(PI-IPI) and poly(2,5-dihydroxybenzene-azomethine-phenyl-azomethine) P(PIOH-IPI) were synthesized via Schiff base condensation reaction [19-21]. The polymers P(PI-IPI) and P(PIOH-IPI) were formed via the mixing of terephthalaldehyde (Tph-CHO) with benzenediamine (DAB) and 2,5-Diaminohydroquinone dihydrochloride (DAH), respectively (scheme 1). The polymerization was carried overnight in acetonitrile and under reflux. The successful synthesis of the polymers was verified from the physicochemical elemental analysis (C, H, N and O) as mentioned in the synthesis section.

The polymers have shown good mechanical stability after filtration and washing exhaustively with HCl (0.1M), NaOH (0.1M), water and acetone. However, the thermal gravimetric analysis (TGA) profiles of the polymers have proven different thermal stability behavior (figure 1A). The polymer P(PI-IPI) is thermally stable up to 340 °C and has shown a weight loss around 100 °C due to the presence of moisture and occluded solvents. However, the polymer P(PIOH-IPI) has a sharp weight loss around 100 °C, which can be attributed to the presence of water molecules coordinated to the OH-sites in the polymer chain. This assumption was supported by the elemental analysis results, which indicated the coordination of at least two water molecules to the polymer chain [22, 23].

Further gradual decrease is resulted from the oxidation and rapid decomposition of the polymer chain. The formation of the imine-bond (-C=N-), the consumption of the (C=O) and the disappearance of the spike band of free –NH_{2} in DAB monomer, were characterized via the infrared spectroscopy (IR) (figure 1B). The imine-bond (-C=N-) appear in the range 1588-1620 cm\(^{-1}\) in the polymers spectra and the disappearance of the stretching frequency at 1720-1750 cm\(^{-1}\) indicated the consumption of the formyl group (CHO) due to the polymerization. The overlapped region around 3000 cm\(^{-1}\) in the polymer P(PI-IPI) when compared with the spectrum of DAB indicated the formation of the imine-bond (-C=N-) (figure S1). The broad band around 3000 cm\(^{-1}\) in the spectrum of P(PIOH-IPI) is resulted from the intramolecular hydrogen-bonding forces [21]. For comparison purposes, the IR spectra of the monomers and polymers are depicted in figure S1 in the ranges 4000-400 cm\(^{-1}\).
Scheme 1. The structures of the polymers P(PI-IPI) and P(PIOH-IPI) and their corresponding monomers (A) Terephthalaldehyde (Tph-CHO), (B) Benzenediamine (DAB), and (C) 2,5-Diaminohydroquinone dihydrochloride (DAH)

Figure 1. (A) Thermal gravimetric analysis (TGA), (B) Infrared spectra in the range 4000-400 cm⁻¹

UV–vis Absorption and Solvatochromism Studies

The electronic spectra of the polymers P(PI-IPI) and P(PIOH-IPI) were collected over the wavelength range of 200-800 nm, in polar-aprotic solvents, DMSO and DMF as shown in figure 2A & B. The absorption spectra have shown two well-defined absorption bands at the wavelength range 260-270 nm and 360-380 nm observed in each spectrum. The former band
may be assigned to the π-π* electronic transitions within the aromatic moiety [24]. The later absorption band can be attributed to an overlapping band of n-π* and π-π* due to the formation of the imine bond (-C=N-) and to the transition of the OH-group. The polymers have shown almost similar absorption bands with notable small blue-shift when the spectra recorded in DMF solvent. This small hypsochromic shift (around 5 nm) is more pronounced in DMF solvent due to the fact that the DMF solvent has higher H-bonding parameter (δH = 11.3) when compared to DMSO solvent (δH = 10.2) as listed in table 1 [25].

Beside the H-bonding parameter of the solvent, the observed blue-shift in polymer P(PI-IPI) is assigned to the presence of the free imine-bond (-C=N-) in the polymer P(PI-IPI), which is accessible for protonation (figure 2 A). On the other hand, a small red-shift of the absorption bands were observed in the case of the polymer P(PIOH-IPI), which is assigned to the presence of the OH-group in the polymer backbone, the formation of the enol-imine tautomer and the extended-conjugated backbone (figure 2B). Moreover, the OH-group is electron-donating substituent that has a resonance effect, which enriches the electron delocalization on the structure and hence resulted in higher wavelength [26]. For comparison, the UV-vis spectra of the polymers and their corresponding monomers were depicted in figure 2.

**Table 1**: The maximum wavelengths (λmax) of the polymers P(PI-IPI) and P(PIOH-IPI) and their band gap values. The band gap determined from the onset of the absorption bands.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>λmax (nm) in DMF</th>
<th>λmax (nm) in DMSO</th>
<th>band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>DMF</td>
</tr>
<tr>
<td>P(PI-IPI)</td>
<td>368</td>
<td>372</td>
<td>2.95</td>
</tr>
<tr>
<td>P(PIOH-IPI)</td>
<td>376.3</td>
<td>380</td>
<td>2.94</td>
</tr>
<tr>
<td>shows two Absorption maxima</td>
<td>395.5</td>
<td>400.9</td>
<td></td>
</tr>
</tbody>
</table>
The pH-sensing capability of the polymers P(PI-IPI) and P(PIOH-IPI) was investigated in DMSO solvent and the results were compared. The polymers in this study reveal an identical structural backbone, except the presence of the OH-group in the case of P(PIOH-IPI). Thus, the aim of this part is to make a comparison between the behavior of the polymers in acidic and basic medium upon the inclusion of the OH-group, via the use of UV-vis absorption measurements. The UV-vis spectra were collected for the polymers (P(PI-IPI) and P(PIOH-IPI)) in an individual mixed solutions of DMSO and 1 mL of 1 M HCl, DMSO and 1 mL of 4 M NaOH and DMSO and buffer solutions (e.g. phosphate buffer) with different pH-values (pH = 1, 4, 7, 10 and 13). As mentioned above, the absorption spectra of the polymers in DMSO have shown a small bathochromic shift due to the lower H-bonding parameter of DMSO when compared to DMF solvent [25]. However, upon adding 1 mL/ 1 M HCl and 1mL/ 4 M NaOH, the polymers have shown significantly different behavior.

P(PI-IPI), which contains the only imine-bond functionality, beside the conjugated aromatic system, was blue-shifted in the acidic medium (1 M HCl), while its absorption band retained in the same region when soaked in the basic solution (4 M NaOH) (figure 4). This observation supported the fact that the imine-bond is basic site and the basic solution had nothing to do with the species presents in the solution. However, in the acidic medium the imine-bond was accessible for protonation and therefore, it is blue-shifted. For further investigations, the UV-vis absorption spectra were collected for the polymer at different pH values and have resulted in blue-shift in the case of pH = 1, 4, while at pH = 7, 10, 13, the absorption bands were almost similar to the absorption of the polymer in DMSO (figure 5). From the above discussion, one can conclude that the presence of the free imine-bond in P(PI-IPI) makes this polymer significantly a responsive material to the acid solutions and perform as the regular polymer in the basic solution.

Interestingly, the absorption spectra of the polymer P(PIOH-IPI) have shown blue-shift and one similar response behavior toward the acidic and basic solutions. Additionally, the absorption spectra of the polymer have illustrated similar blue-shift, around 300 nm, upon changing the pH values. In general, the above observations can be related to the presence of the OH-group in the structural backbone of the polymer. Going back to the polymer structure, each monomer of the extended-chain of P(PIOH-IPI) contains two phenyl rings connected via
the imine-bond. One of the phenyl rings has para-OH groups, each appears at the ortho-position to the ring connected to the N atom of the imine-bond (-C=N-), while the second phenyl is non-functionalized (scheme 2 A). Thus, the oxygen of the OH-group plays a role of an H-donor and the nitrogen of the imine-bond can be the acceptor.

A similar computational study [29], on OH-substituted benzylidene Schiff bases molecules, which has the components of P(PIOH-IPI) (scheme 2 A), have indicated that the position of the OH-substituent on the ring influences the spectroscopic properties of the molecules. The structural a feature that reveals the OH-group at the ortho-position to the carbon of the imine-bond (scheme 2 C), has a quasi-six-membered ring H-bonding intramolecular interactions, broad band in the IR region (figure 1 B) and shoulder band in the UV-vis above 400 nm due to the formation of keto-amine tautomer [29]. On the other hand, when the OH-group located at the ortho-position to the nitrogen of the imine-bond (scheme 2 B), the H-bonding appear as a quasi-five-membered ring, which indicate a weak H-bonding interaction. This attraction is less favored when compared to the quasi-six-membered ring and has a moderate stability [21].

In the same manner, it has been reported by others that the ortho-OH play a role of electron-donation group and create a resonance (electron-delocalization) [30] on the structure, which also shift the band to a higher wavelength. Consequently, the UV-vis absorption, which is assigned below 400 nm can be attributed to the presence of enol-imine tautomer only and the absorption shoulder-band above 400 nm in the polymer P(PIOH-IPI) is due to the substituent effect rather than the possibility of keto-amine tautomer formation. This kind of reported results have encouraged us to expect that the notable red-shift above 400 nm is assigned to the presence of OH group as donating group rather than the keto-amine tautomer formation and the band below 400 nm is attributed to the enol-imine tautomer form of the polymer and the formation of a polyaromatic conjugated system in the backbone [21, 30, 31]. Furthermore, the observed significant blue-shift in the acidic medium can be resulted from the protonation of the imine-nitrogen atom, while, in the basic medium, the role of oxygen as proton donor become crucial and cause the de-protonation and therefore stabilized by the resonance effect of the electron-donating OH-group.
Figure 4. UV-Vis absorption spectra of the polymers in DMSO, 1 M HCl and 4 M NaOH, (A) P(PI-IPI), (B) P(PIOH-IPI) and the spectra at different pH values (C) P(PI-IPI), (D) P(PIOH-IPI).

Density Functional Theory Computational Calculations (DFT):

In our previous report [18], we have, theoretically, calculated the HOMO, LUMO and band gap of the synthesized polymers by using DFT method operated in the gas phase. However, the obtained band gap results were overestimated when compared with the experimentally determined values from UV-vis. Accordingly, we have concluded that the large difference in the experimentally and theoretically determined $\lambda_{\text{max}}$ is attributed to the absence of the solvent effect, inter- and intra-molecular attraction forces and for more compatible results, the solvent effect has to be taken into account. Herein, to overcome the above limitation and as a part of our ongoing studies, we have performed the DFT calculations, on the polymers P(PI-IPI) and P(PIOH-IPI), by considering the gas phase and solvent effect (e.g. DMSO) and compared the results. Additionally, from the optimized structures of the polymers, we have investigated the impact of the substituent (OH-group), structure conformation (e.g. cis, trans) and length of conjugation on $\lambda_{\text{max}}$ and the calculated the band gap of the polymers.

The theoretical calculations were carried out using the Gaussian09 package [32], and performed the DFT calculations. The basis sets applied here is 6-311+G(d), has polarization, diffuse functions and allow intramolecular interaction description (e.g. H-bonding) that are suitable and flexible to study the polymers in this work. To investigate the infinite unit of the
polymers, we have employed the periodic boundary condition (PBC) model and assign the discrete MO model in the continuous bands. We have also, optimized the (PBC) model polymers and then calculated the band gap difference between the HOMO and LUMO orbitals.

DFT Calculations Results

The DFT calculations performed in this work aims at rationalizing and predicting the maximum wavelength (λmax) of the polymers P(PI-IPI) and P(PIOH-IPI) upon the inclusion of OH-substituent OH-group, at different chain conformation and lengths of conjugation. All calculations were demonstrated under the effect of DMSO solvent and gas-phase. The calculations have indicated the presence of cis and trans conformations of each polymer. For simplicity, in this part, we have discussed the effect of DMSO solvent and the gas-phase on the UV-vis spectra of the cis-conformer of the polymers and determined their λmax (table 2). Compared to the gas-phase, the calculations performed in DMSO solvent have shown a large bathochromic shift of λmax values (Figure 5 A & B). In a similar study, this observation was attributed to the stabilized exited electronic structure under the solvent effect. On the other hand, the notable hypsochromic shift (shift-down by 10-15 nm) in the gas phase is generally, related to the absence of solvent effect and a large gap between HOMO-LUMO energy levels.

![Figure 5. UV-vis spectra of the polymers, exp (in DMSO) and from DFT calculations in the gas-phase and DMSO solvent. (A) P(PI-IPI), (B) P(PIOH-IPI), (C) Area (370-420 nm), (D) Area (330-430 nm).]
Interestingly, the performed experimental and theoretical UV-vis spectra of the polymer P(PI-IPI) in DMSO were in good agreement with about 5 nm difference. However, the calculated spectra of P(PIOH-IPI) have shown two well-defined maxima, while the experimentally measured spectra revealed one clear maxima beside a barely notable shoulder (Figure 5 C, D). The λmax value around 400 nm is corresponding to the presence of OH-group. The electron-donating effect of The OH-substituent, enrich the ring of electron-delocalization and hence increases the λmax value.

**Table 2.** Theoretical and experimentally determined λmax values of the polymers and their calculated band gaps.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>λmax Gas-phase</th>
<th>λmax DMSO solvent</th>
<th>Band gap (eV)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(PI-IPI)</td>
<td>362.4</td>
<td>Exp: 372.7</td>
<td>DFT: 377.7</td>
</tr>
</tbody>
</table>

*Band gap of the cis-monomers optimized in DMSO solvent. The polymer reveal two λmax*

The optical band gaps of the polymers were calculated from the optimized structures in the DMSO solvent and summarized in table 2. Further factors that affect the optical band gap, are the structural conformation and the length of conjugation [33]. From the optimized structures of the polymers, the structure of the monomers corresponding to P(PI-IPI) and P(PIOH-IPI) have shown two minima conformation structures; cis and trans, with small energy differences 0.28 kcal/mol, and 2.8 kcal/mol, respectively. The UV-vis spectra of the conformation have shown a similar shape of the absorption bands when compared to the corresponding polymers (figure 6). The λmax values and the band gap of the cis and trans conformers of P(PI-IPI) and P(PIOH-IPI) from the gas phase and DMSO are illustrated in figure 7 and table S2. The band gap of the polymer P(PIOH-IPI) is decreased by 0.38 eV when compared to the polymer P(PI-IPI). This difference can be accredited to the inclusion of the OH-substituent in the polymer chain (figure 8). The presence of the OH-substituent leads to a significant change on the electronic structure of the polymer due the electron-delocalization (resonance effect) and lower the band gap [34, 35].
Effect of the Length of conjugation on the band gap

In this section, we have studied the pronounced effect of the length of conjugation on the optical band gap by evaluating the monomer, dimer and tetramer structures of the cis-conformers of the polymers P(PI-IPI) and P(PIOH-IPI) using DFT calculations. In general, a red shift has been observed in the UV-vis spectra of the dimer and tetramer up to 462 and 509.7 of the polymer P(PI-IPI). In the same trend, the higher wavelength of the monomer structure of P(PIOH-IPI) is 433 nm and has been shifted up to 498 and 539 in the dimer and tetramer, respectively (figure 7). It is noteworthy that the two absorption maxima were merged in one band in the case of the tetramer structure, which can be accredited to the twisted structure and loses of conjugation. Nevertheless, the spectra of the monomers of both polymers have shown a good match with the experimentally measured spectra (figure 7).

Interestingly, these results are supported by the previous study that studied the impact of extended conjugation on a substituted and non-substituted oligo- and polythiophenes [34]. One of the significant outcomes from this study has concluded that the width of the HOMO-LUMO gap (band gap) decreases with increasing size of the oligomer and the inclusion of electron-donating substituent. The optimized structures of the monomer and dimer of the polymers are shown in figure 8, and the band gap values were summarized in table 3.
Moreover, to investigate the infinite unit of the polymers, we have employed the periodic boundary condition (PBC) model and assign the discrete MO model in the continuous bands. We have also, optimized the (PBC) model polymers and then calculated the band gap difference between the HOMO and LUMO orbitals. The PBC model of the polymer P(PI-IPI) has shown the lowest band gap due to the considered infinite chain. The results also were consistent with the optimized tetramer and PBC model of the polymers (figure S5). The error between the calculated and experimental values is could be related to several reasons such as the planarity, conformation, and the use of finite chain for calculations and regular infinite chain in the real experiments. Thus, the experimentally calculated band gap support the fact that the polymer chain is not rigid beyond the monomer, and the twisted structure might lead to the conjugation-chain loose (less effective conjugation) and hence higher the band gap values of the calculated structures.

Figure 7. The UV-vis spectra of the monomer, dimer, and tetramer of cis-conformers and the experimentally determined spectra of (A) of P(PI-IPI), (B) P(PIOH-IPI) in DMSO solvent.

Table 3. The calculated band gap values (eV) for the monomer, dimer, tetramer and PBC.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Exp (Eg)*</th>
<th>Monomer</th>
<th>Dimer</th>
<th>Tetramer</th>
<th>PBC*</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(PI-IPI)</td>
<td>2.87</td>
<td>3.62</td>
<td>3.10</td>
<td>2.82</td>
<td>2.64</td>
</tr>
<tr>
<td>P(PIOH-IPI)</td>
<td>2.92</td>
<td>3.24</td>
<td>2.91</td>
<td>2.73</td>
<td>2.56</td>
</tr>
</tbody>
</table>

(A) LUMO

Eg = 3.62 eV

HOMO

Monomer P(PI-IPI)

Dimer P(PI-IPI)
CONCLUSION

To summarize, we have successfully synthesized and fully characterized two imine-linked polymers named P(PI-IPI) and P(PIOH-IPI) that reveal the same structural backbone, while the polymer P(PIOH-IPI) is functionalized with hydroxyl-groups. The polymers have shown acceptable thermal stability behavior in the range 100-300 °C. The polymer P(PI-IPI) is a good candidate for sensing applications due to its basic nature which responds to the presence of acids at different pHs and concentrations. However, upon the functionalization of the OH-group, there was a notable shutdown of the distinguished sensing behavior of the polymer P(PIOH-IPI). We have also examined the electronic properties of the polymers in different solvents, acidic and basic mediums. From the UV-vis spectra, the polymers have shown tailored band gap values upon soaking the polymer in acidic, basic, different solvent mediums. Furthermore, the band gap of the polymers was calculated by applying the density functional theory (DFT) on the cis- and trans- conformations, monomer, dimer, tetramer and PBC model of each polymer. The calculated band gap values were agreed with the experimentally determined values, while the error is attributed to the determination method. The values calculated upon changing the length of the optimized chain have supported the fact that: the band gap decreased with the increased length of the chain which also resulted in loss of planarity and hence the loss of conjugation. In general, the inclusion of electron-donating functional group such as, OH-group on the polymer chain, would red-shift the absorption, decreased the band gap and tailors the polymer behavior.

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