Synthesis, Experimental and Theoretical Study of Imine based Conjugated Polymer for Humidity Sensing Applications

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Abstract

A donor-acceptor conjugated polymer was synthesized by poly-condensation reaction of dialdehyde and aromatic diaime. The characterization of polymer was done by UV-Vis, FT-IR, ^{1}H NMR spectroscopic techniques. The obtained polymer was found to be partially soluble inorganic solvents such as chlorobenzene, DMF. The polymer was found to be responsive to humidity, which varied its electrical properties on exposure to humidity, arising due to protonation of imide nitrogen in polymer backbone. Further, Theoretical studies using density functional theory (DFT) were performed on the polymer to optimize the geometry, verify the proposed experimental sensing mechanism and also to understand its photophysical properties. The theoretical results showed good agreement with the experimental values. Humidity sensing properties like response-recovery and the reproducibility of the polymer were also studied. The research findings showed that the new polymer is promising material in moisture sensing application.

Keywords: DFT method, Imine linkage, Donor acceptor, moisture sensor

1.0 Introduction

The ability of conjugated polymers (CP) to interact with various analytes resulting in changes in their photo physical properties have been explored by the scientific community extensively for sensing various toxic gases such as NH_3, NO_2, CO_2, CO, HCl and volatile gases like alcohol and in humidity sensing applications [1-4]. These conjugated polymer-based sensors are more imperative as compared to metal oxide-based sensors due to their faster response and recovery, ease of fabrication and ability to operate at room temperature. Recently, humidity sensors have gained increasing applications in both industries, in environmental control as well as in house-hold equipment's like microwave ovens, washing machines etc. Based on the measurement units, there are two types for humidity sensors Relative Humidity (RH) sensors and Absolute humidity (moisture) sensors. Most humidity sensors are relative humidity sensors and can be further classified based on the materials used for the development of sensors into ceramic sensing materials, semi-conducting

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materials and polymer-based humidity sensors [5]. Most of the commercial humidity sensors available in the market are resistive based humidity sensors [6]. The material used for sensing may be ceramic, polymers or electrolytes. They display change in the conductivity due to adsorption of water vapor [7]. Conjugated polymers emerge as promising materials for humidity sensors. They have presence of unsaturation or double bonds and offer flexibility in controlling their band gap by substituting various donor (D) acceptor (A) moieties which dictates the electrical and optical properties of the polymer. Water can easily protonate these double bonds and shows changes in the conductivity. Conjugated polymers like polyaniline have been previously reported to be used as humidity sensors. Polyaniline and its composites with zinc oxide, magnesium chromate[8], doped with acids [9], PANI-chitin blend[10] have also been reported as humidity sensors. Additionally, Poly pyrrole and its composites have also been studied in humidity sensors[11 - 12].

Considering the above, we report the synthesis of polymer P, bearing a surplus of phenylene group. The polymer P proved to be a potential candidate for humidity sensing with high response for which the sensing mechanism was studied. Optical and electrical properties of polymer P was experimentally studied using UV, FT-IR and NMR techniques. Additionally, theoretical calculations were performed using density functional theory (DFT) and time dependent DFT (TDDFT) to characterize the photophysical properties such as HOMO-LUMO, band gap and UV-vis spectra of polymer P and to elucidate the response mechanism of the polymer towards humidity sensing.

2.0 Experimental Work

2.1 Synthesis of polymer P

The Octyl diphenylamine dialdehyde (ODPADA) monomer was synthesized according to reported literature [13]. Polymerization of N-Octyl diphenylamine dialdehyde (ODPADA) with p-diamino diphenyl (Polymer P) Condensation polymerization of Octyl diphenylamine dialdehyde (ODPADA) with 1,4 diphenylene diamine was carried out using anhydrous methanol as the solvent. For this, both the monomers, dialdehyde (0.00297 mole) and 1,4 diphenylene diamine (0.00297 mole) each one equivalent were mixed with each other in 25 ml of methanol in a round bottom flask. On formation of homogeneous solution, 2 drops of concentrated sulfuric acid were added which immediately resulted in formation of a dark red colored precipitate. The polymerization reaction was carried for 4 hours at room temperature. After 4 hours, polymerization was terminated by pouring in ice cold water and then filtering the product through Buchner funnel. The impurities present in the polymer i.e. polar and non-polar were removed by stirring the polymer in hexane and ethyl acetate solvents followed by decantation. Thus, the obtained precipitate was dried under ambient conditions and is as shown in Scheme 1.

Polymer P was partially soluble in the organic solvents like chlorobenzene, DMF, DMSO etc. The partial solubility may be due to the increased molecular

weight of the polymer. The polymer showed high thermal stability may be attributed to the presence of aromatic phenyl rings. Due to partial solubility of the polymer, thin films on the glass plate were prepared by solid state method. For this, solid polymer powder was ground with few drops of DMF in a mortar and pestle and then cast on the glass plate.
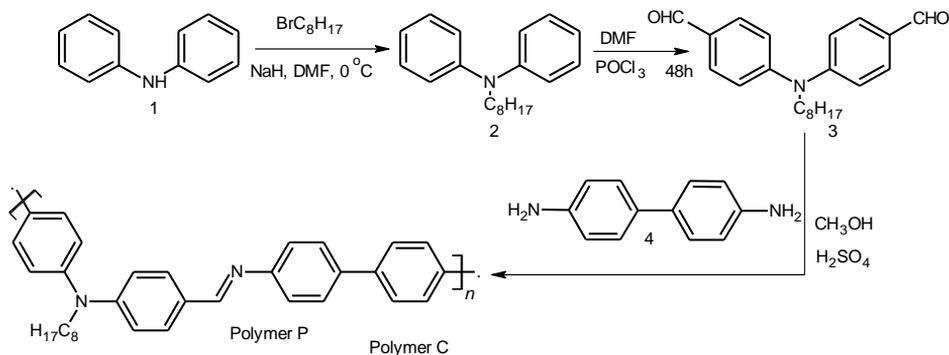
Scheme 1: Synthesis of Polymer P

3.0 Material Characterization

3.1 Materials

Dialdehyde monomer was synthesized according to the reported procedure[13]. All the chemicals used in present work were procured from Sigma Aldrich and Lanchaster (UK). All the solvents purchased were of analytical grade and was used as such without any further purification.

3.2 Instrumentation

Infrared spectra of all compounds and polymer were recorded using Nicolet Avatar 5700 FTIR (Thermo Electron Corporation). The UV-visible spectrum was recorded in Perkin Elmer LS55. ^{1}H NMR spectra were obtained with Brukere 400 MHz FT-NMR spectrometer using TMS/solvent signal as internal reference.

3.3 Characterization

FTIR spectroscopic study of the polymer showed strong bands at 2927(Aromatic C-H stretch), 2848, 2600(Broad C-N stretch), 1575(C=C stretch), 1497, 1353(=C-N stretch), 1136(-C-N stretch), 1029, 801. Disappearance of carbonyl stretching frequency from 1685 cm^{-1} from the dialdehyde monomer indicates that the formyl group involved in polymerization reaction. Also formation of peak at 1353 cm^{-1}represents the formation of imine linkages in the polymer backbone as represented in Fig. 1.
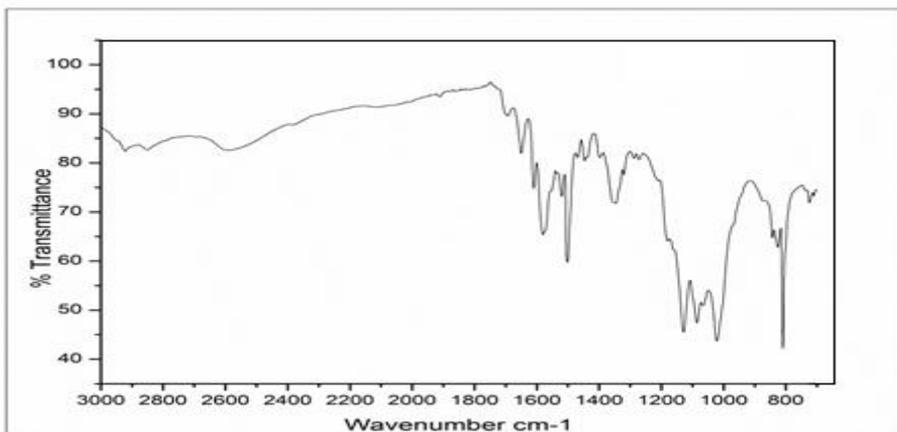
Fig.1. FT-IR spectrum of Polymer P

The NMR spectral study of the polymer showed chemical shifts at 7.89-7.3δ (m)(Benzyl H), 7.27-7.1 δ (m)(Benzyl H), 6.65, 6.62 δ (s) (-N=CH), 3.82 δ (t)(N-CH$_2$) ,1.62 δ (m)(- CH$_2$-) , 1.18 δ (m)(- CH$_2$-)0.79δ (t)(-CH$_3$). Disappearance of aldehydic proton from the monomer clearly indicates that the polymerisation reaction is happened with the monomer. Also appearance of new –N=CH- chemical shift at 3.82δ indicates the formation of imine functionality in the polymer bbackbone and it is represented in Fig. 2.
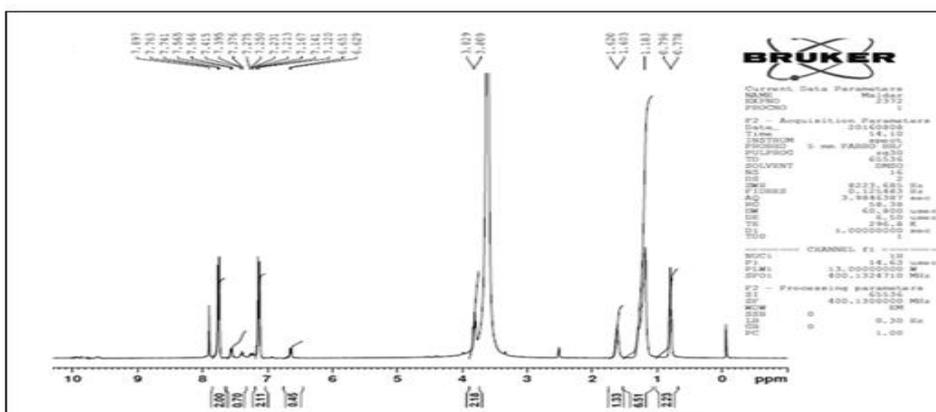
Fig. 2. NMR spectrum of Polymer P

3.4 Optical study of the polymer

UV-Visible spectral study of the polymer was done in thin films. Thin films are casted on glass surface and taken for study. The absorption maximum of polymer was found to be 350 nm in film state **Fig. 3**. The optical band gap was calculated by using optical edge and was found to be 3.04 eV. The broad absorption of the polymer may be attributed to its donor acceptor nature and conjugation due to imine linkage.
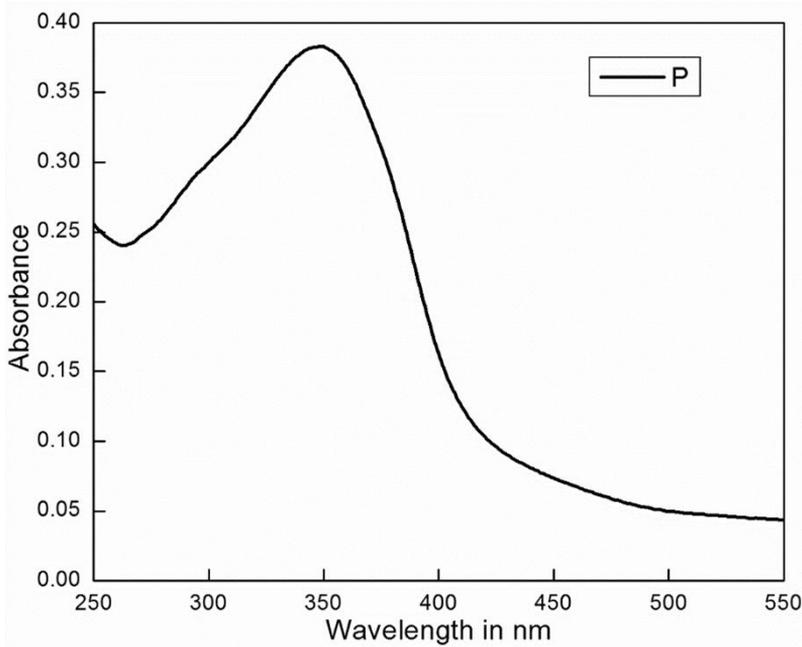
Fig. 3. UV-Visible spectrum of Polymer P in film

4.0 Computational Details

The theoretical computational studies on Polymer P were performed using density functional theory (DFT) to optimize the geometry and to understand the humidity sensing mechanism by the polymer. To reduce the computational cost, a single repeating unit of the polymer is considered for computations and the alkyl side chains were replaced by propyl chains. The geometries of polymer P and polymer P-H_2O complex were optimized using Becke's three parameter hybrid functional [14] with the Lee, Yang, and Parr correlation functional (B3LYP) using the Pople basis set, 6-31G(d) [15], in THF solvent. The dispersion interactions effects were also included using Grimme's DFT-D3(BJ) method. Further, the photophysical properties of polymer were calculated utilizing time dependent DFT (TDDFT) at B3LYP/cc-pVTZ level of theory in THF solvent incorporating CPCM solvent model. The humidity sensing mechanism of polymer was theoretically elucidated by interpreting the intermolecular bond lengths between host and guest molecule and variation in photophysical properties of polymer P and its complex. All the theoretical calculations were performed using ORCA 4.0.1 platform [16].

5.0 Results and Discussion

5.1 Humidity sensing of polymer P.

It has been well reported that saturated salt solutions, at a given temperature, in an enclosed environment generate an environment of particular relative humidity. The generated relative humidity depends upon the particular salt

used[17], [18] . Relative humidity (RH) is defined as the amount of moisture content of air to the amount of the saturated moisture content of air at the same temperature and pressure[5], [7]. The RH%= Pv/Ps where Pv= Actual partial pressure of moisture content And Ps= Saturated pressure of moist air.

Thus, different saturated salt solutions (solid salt present) were prepared from chemically pure salt and distilled water in a sealed glass chamber and allowed to stabilize for 24 hours at room temperature. The solutions are as shown in the Fig. 4. At a specific temperature, different relative humidity in an enclosed space for a given salt solutions is known. Using the same, we have generated different relative humidity in the closed chamber for a specific salt solution and sensor measurements of the polymer P in this environment was successfully initiated. We have measured the response of polymer P at different relative humidity values and they are as reported in Table 1 and the graph of % response vs % relative humidity is as depicted in Fig. 5. Polymer P shows very good response (58%) even towards low relative humidity of 8.3%. The response increases drastically from 58% to 91.1% by increasing the relative humidity from 8.3% to 22.5%.

Fig. 4. Saturated salt solutions corresponding to different relative humidity

Table 1. Response of Polymer P on exposing to different relative humidity

Sl. No.	Chemical	Relative Humidity	Initial resistance (G Ohm)	Final resistance (G Ohm)	Response Time (sec)	Recovery Time (sec)	Diff resistance (G Ohm)	% Response
1	KOH	8.3	34	14	50	59	20	58.8
2	CH_3COONa	22.5	30	2.66	61	105	27.34	91.1
3	$CaCl_2$	32	22	1.95	68	110	20.05	91.1
4	K_2CO_3	43.2	32	2.3	94	123	29.7	92.8
5	$Mg(NO_3)_2$	57.6	24	2.4	77	112	21.6	90.0

6	NH_4NO_3	64	28	2.6	73	102	25.4	90.7
7	KI	68.8	35	3.2	61	83	31.8	90.9
8	NaCl	75.3	30	2	67	92	28	93.3
9	KCl	84.3	33	2.2	57	48	30.8	93.3
10	KNO_3	94	32	0.74	122	121	31.26	97.7
11	K_2CrO_4	97.88	32	1.01	60	84	30.99	96.8
12	K_2SO_4	97.3	32	0.55	83	111	31.45	98.3
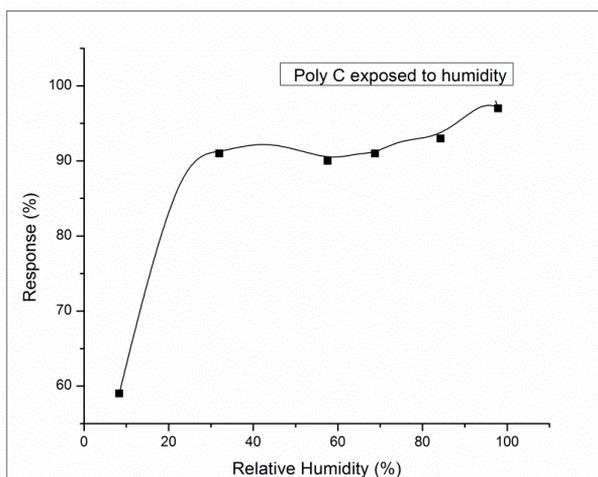
Fig. 5. Response of Polymer P at different relative humidity

5.1.1 Proposed mechanism for humidity sensing

Polyaniline shows non-redox doping by protonation. Water is also able to protonate PANI and its mechanism is well established. Imine nitrogen in PANI undergoes protonation due to which the resistance of polyaniline decreases[17]. On exposing polymer P to different relative humidity's, it has been observed that its film resistance decreases. This decrease in the resistance can be attributed to the protonation of H in to the polymer matrix. This protonation of imine nitrogen is very much similar to protonation which takes place in polyaniline. The decrease in resistance of polymer film is as shown in Fig. 6 and the probable mechanism displayed in Fig. 7.
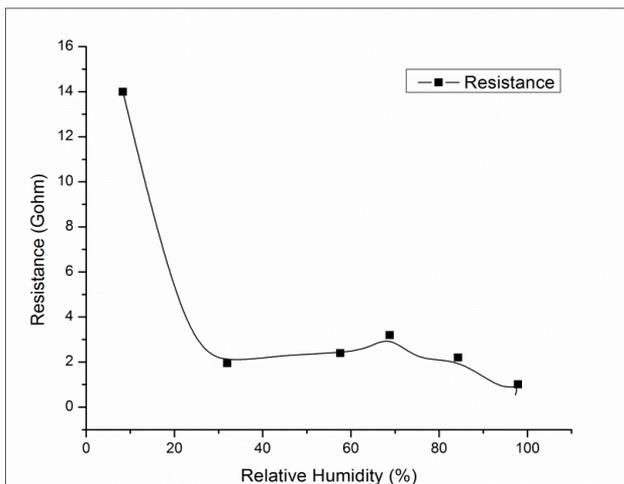
Fig. 6. Decrease in resistance of Polymer P at different relative humidity values
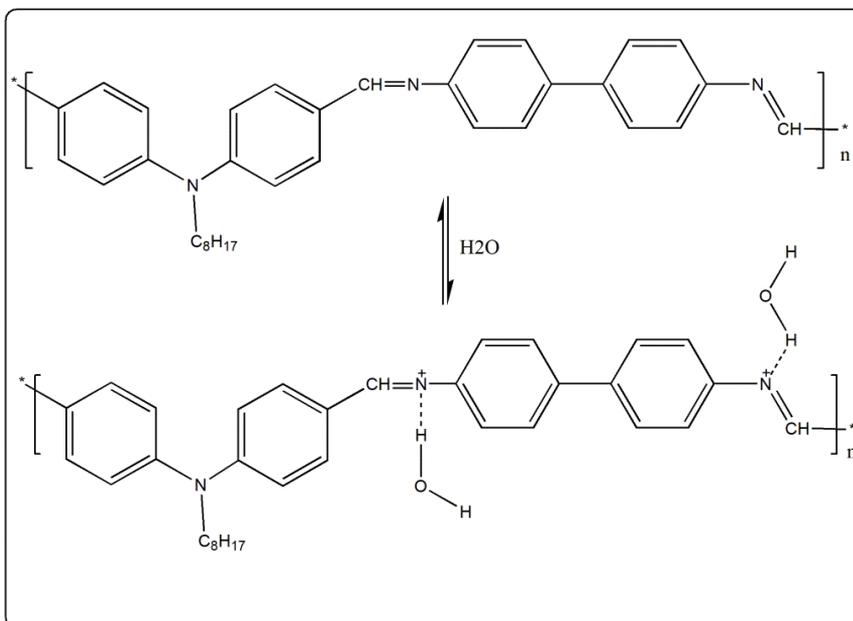
Fig. 7. Mechanism of protonation for Polymer P

The response and recovery time for the polymer film was also studied. The graph is as shown in Fig. 8. Both response and recovery time initially increased and then decreased. These observations happened rapidly between 1-2 min.
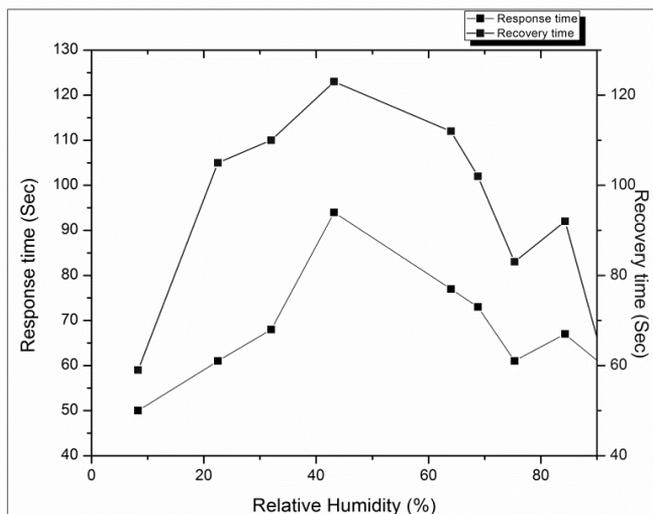
Fig. 8. Response- recovery studies of Polymer P at different relative humidity

5.2 Quantum chemical calculations

The geometry optimization of polymer P and its complex with water molecules was performed using DFT at B3LYP/6-31G(d) level of theory in THF solvent. The respective optimized structures are depicted in Fig. 9-10. The protonation sites on polymer backbone due to its interaction with water molecules were considered as suggested by experimental mechanism for the optimization of its complex state geometry. From Fig. 10 it can be noted that in the presence water molecules, the polymer forms hydrogen bond with the nitrogen atoms with bond lengths of 0.977Å and 1.221Å. These interaction bond lengths are comparable to the covalent bond length of N-H in the system, thus confirming the protonation of polyaniline.
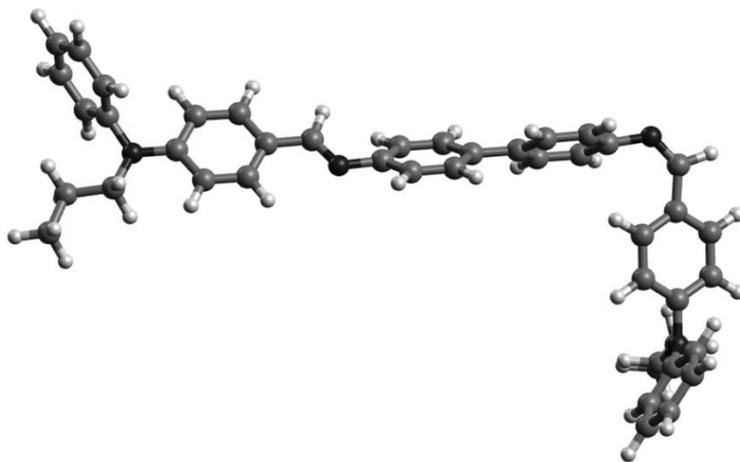
Fig. 9. Optimized geometry of polymer P at B3LYP/6-31G(d) in THF solvent
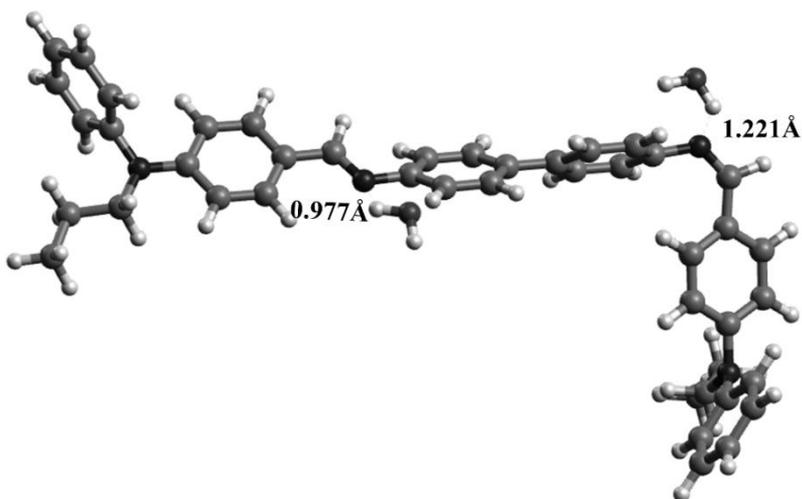
Fig. 10. Optimized geometry of polymer P + water complex at B3LYP/6-31G(d) in THF solvent

The Mulliken charges of polymer P were calculated at the same level of theory which is depicted in Fig. 11. From the bar graph it can be noted that the nitrogen atoms in the ground state geometry showed higher negative charge values indicating that these are the potential sites for protonation, and all the hydrogen atoms showed almost equal positive charge values.
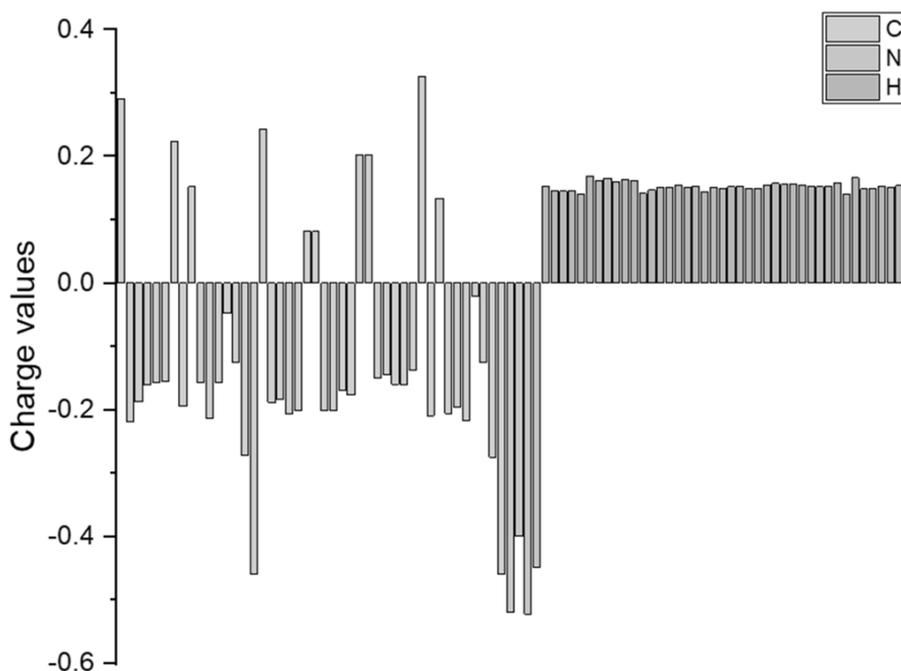
Fig. 11. Mulliken charge values of polymer P at 6-31G(d) level of theory

The frontier molecular orbital density plots of polymer P is visualized in Fig. 12. From the theoretical calculations the HOMO and LUMO values were found to be -5.269 eV and -1.795 eV respectively having a theoretical HOMO-LUMO energy gap of 3.47eV which is in good agreement with the experimental value (3.04 eV). From Fig. 12 it can be noted that HOMO orbital density is distributed over the entire monomer unit and LUMO orbital density localized over diphenylene ring, dictating the effective charge transfer across D-A system.
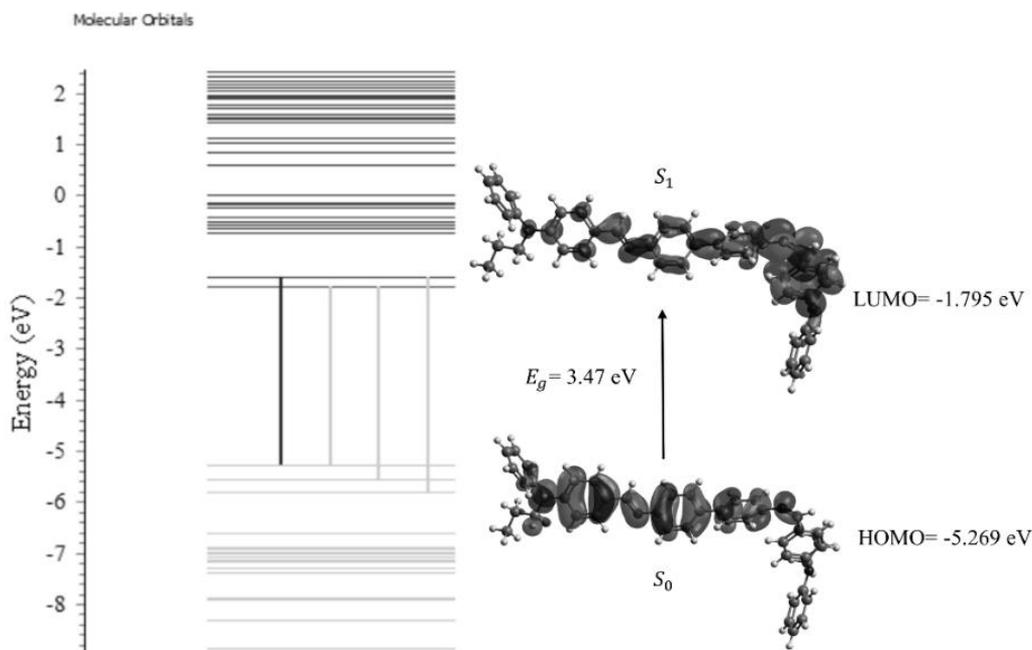
Fig. 12. HOMO-LUMO energy of polymer P in THF solvent (isovalue=0.02)

Table 2. Photophysical properties of Polymer P.

Major transitions[*]	Energy (cm^{-1})	Osc. Strength (f)	λ_{max} (nm) theoretical	λ_{abs} (nm) experimental
H→L+1 (78%)	26656.5	1.3762	375.14	350
H-1→L (77%)	21953.6	0.1332	455.50	-
H→L (75%)	21811.7	0.4295	458.47	-

H denotes HOMO and L denotes LUMO
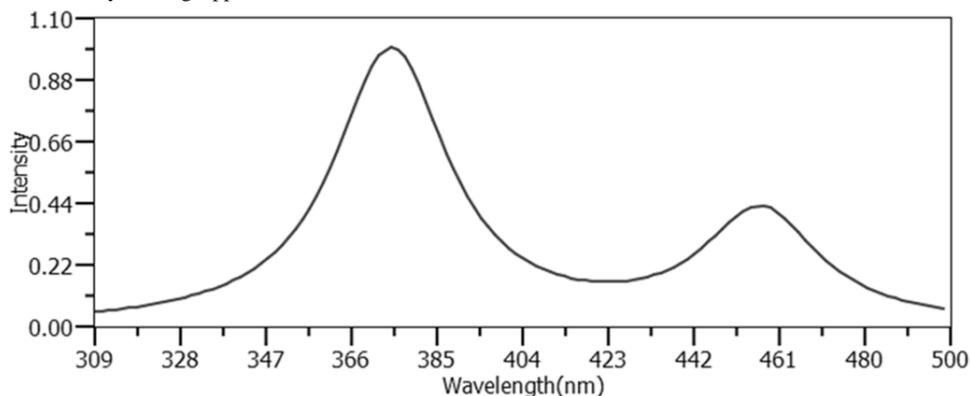
Fig. 13. Theoretical UV-vis spectra of polymer P

The theoretical optical and electronic properties of polymer P was studied employing time-dependent density functional theory (TDDFT) at B3LYP/cc-pVTZ level of theory in THF solvent system incorporating CPCM model. The above optimized geometry was used for TDDFT calculation. The major orbital transitions, oscillator strengths and absorption wavelengths are summarized in Table 2. The polymer P showed an absorption peak at 375.14 nm (Fig. 13) contributed by transition of HOMO→LUMO+1 (78%) having an oscillator strength of 1.3762. The theoretical calculations showed good agreement with the experimental values hence the polymer may be a potential candidate for humidity sensing.

6.0 Conclusion

A new donor acceptor conjugated polymer containing iminebridge was successfully designed and synthesized via poly condensation reaction. The structure of monomer and polymer were characterized by various spectroscopic techniques. The newly synthesized polymer showed absorption maximum at 350 nm with the optical band gap of 3.04 eV. The polymer films were casted on glass plate and used for sensor studies. Polymer showed very good response (58%) even with very low relative humidity of 8.3%. The response of polymer films increased drastically from 58% to 91.1% by increasing the relative humidity from 8.3% to 22.5%. The sensor response mechanism of polymer towards moisture may be due to the hydrogen bonding interaction. Further theoretical DFT studies of the polymer were in good agreement with the experiment results. Optimized geometry of polymer P + water complex showed clear evidence for bonding interaction between from theoretical study. The Sensing studies were showed enhanced response and recovery time. This may be attributed to the porous nature of the polymer which slows down the adsorption and desorption process on the surface of the sensor.

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