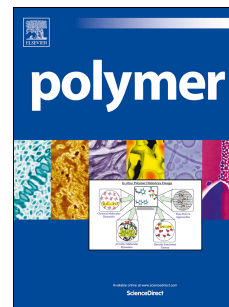


# Accepted Manuscript

Synthesis and experimental investigations on the photoconductivity of *p*-aminoazobenzene based non-conjugated polybenzoxazine system

Jisha J. Pillai, Anshad Abbas, Sona Narayanan, K. Sreekumar, C. Sudha Kartha, Rani Joseph



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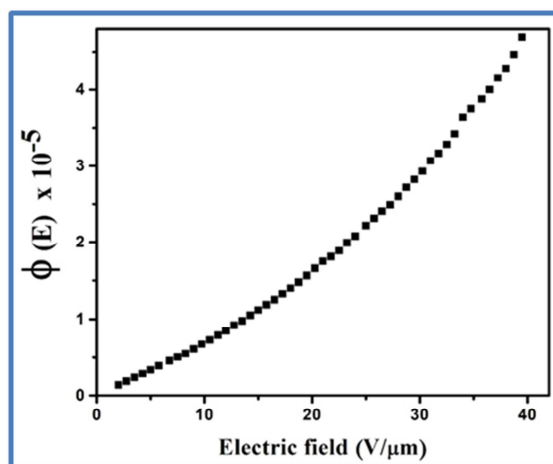
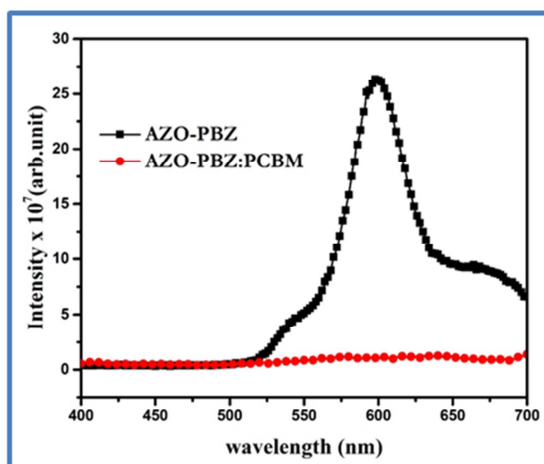
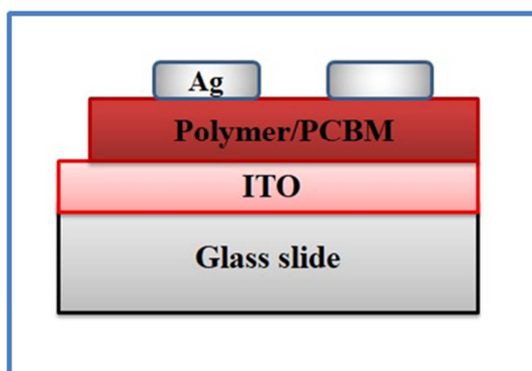
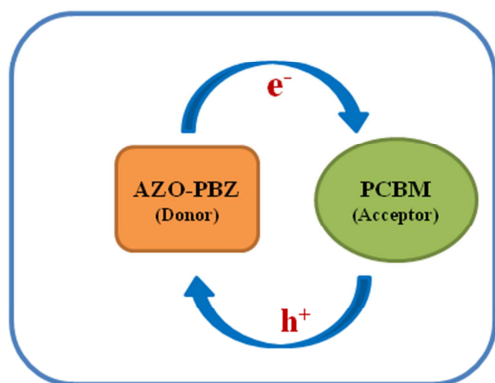
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# Synthesis and experimental investigations on the photoconductivity of p-Aminoazobenzene based non-conjugated polybenzoxazine system

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## Abstract

In this paper, we report the study of a novel p-aminoazobenzene based non-conjugated, benzoxazine polymer, poly([4-(6-tert-butyl-4*H*-benzo[e][1,3]oxazin-3-yl)phenyl]-phenyldiazene) (AZO-PBZ) synthesized using solvent free, thermally activated cationic ring opening polymerization. The thermal, photophysical, electrochemical, and photoconducting properties of the polymer were investigated. The optical absorption band edges of AZO-PBZ thin film was observed at 555 nm. Photoinduced charge transfer nature of AZO-PBZ was studied by analyzing the fluorescence spectra and performing photoconductivity experiments. Incorporation of [6, 6]-phenyl-*C*<sub>61</sub>-butyric acid methyl ester denoted as PCBM into the polymer leads to quenching of the fluorescent intensity and exhibits significant photoconductivity. The photocurrent through the PCBM blend films was measured as a function of electric field to recognize the field dependence on carrier generation. Internal photocurrent efficiency of the polymer:PCBM blend samples was found to be in the order of 10<sup>-5</sup> and photoconductive sensitivity was of the order of 10<sup>-11</sup> S W<sup>-1</sup>cm, which is adequate for photorefractivity.

**Keywords:** *polybenzoxazine, cationic ring opening polymerization, photoconductivity, donor-acceptor polymer*

## 1. Introduction

In the past few decades, macromolecules with unique combination of both electronic and optical properties have gained considerable attention in the field of optical storage media, dynamic holography, photorefractive composites, photovoltaic and photoconducting devices due to increasing need for low cost materials with structural flexibility, stability and processability [1–4]. Despite a handful of reports on the synthesis and photoconducting properties of conjugated polymer systems [5–7], only very few reports can be found in the literature on non-conjugated polymers. Polybenzoxazines are such kind of polymers with non-conjugated skeleton with benefit of inexpensive precursors including phenols, primary amines and formaldehyde as an asset. The extraordinary molecular design flexibility together with the unique properties such as, low cost, low water absorption, absence of byproducts, no need of catalyst, ease of synthesis etc. make them highly attractive for future applications enabled them to be used in various fields like aerospace, automotive industries, optical storage etc.[8–11]. Another remarkable

characteristic of benzoxazines is their undemanding polymerisability without the presence of a catalyst or solvent at temperatures between 160- 240 °C [12,13]. Ishida et al proposed the ring opening polymerization of benzoxazine which proceeded through a cationic mechanism. The final polymer obtained may have the structure of phenoxy, phenolic or both depending on the polymerization conditions [14–17]. But the ring opening polymerization requires high temperature which may result in the degradation of the polymer [18]. Aniline based photoconducting polybenzoxazine was synthesized and its Photophysical and electrochemical behavior was well explained elsewhere. The band gap of aniline based polybenzoxazine has been reduced by experiencing intramolecule donor-acceptor concept in order to enhance its photoconducting behavior [19]. Photoconductivity in polymeric systems is a complex process involving absorption of radiation, generation of charge carriers, transport, recombination and trapping [20–23]. The charge transport and photoconducting properties of these materials whether it is conjugated or non conjugated, mainly depend on the structure and morphology of the polymer chains.

The present paper reports the synthesis, characterization and photoconductivity studies of Mannich phenolic type, p-aminoazobenzene based polybenzoxazine. Compared to previous reports, higher molecular weight polymer was obtained by adopting in situ polymerization without separating the monomer during the course of reaction [13]. Kishore *et al.* conducted the photoconductivity studies on a series of polybenzoxazine systems and reported that the incorporation of C<sub>60</sub> resulted in an enhancement of photoconductivity [24]. The insolubility of C<sub>60</sub> results in phase separation which in turn adversely affects the performance of device parameters. To overcome such insolubility issues of C<sub>60</sub>, PCBM was used as sensitizer in the present study which is a soluble derivative of fullerene having high electron affinity, mainly used for spectral sensitivity in the visible region [25]. The large value of photoinduced birefringence, photoinduced isomerization, non linear absorption and molecular re-orientation, makes azo polymeric systems an important candidate for optical storage and processing applications [26]. The synthesis and characterization of benzoxazines, prepared by incorporating azobenzene chromophoric groups into benzoxazines was reported earlier [27]. With the advantage of design flexibility and cost effectiveness a modified version of polybenzoxazine based on azobenzene will be a better alternative for the present scenario. The role of azo group on photoconductivity properties of the system was understood by using p-aminoazobenzene as primary amine moiety by attaching this group to the polymer backbone. Here the effect of PCBM as electron acceptor on the photoconductivity of the azo polymer was also carried out as in reports [28]. Also, photogeneration efficiency was calculated by monitoring the intensity and electric field dependence of photocurrent was measured for the polymer-PCBM blend.

## 2. Experimental Section

### 2.1. Materials

All the solvents were purified according to standard procedures prior to use. The following chemicals were used as received without further purification: 4-tertiary butyl phenol (97%, Acros Organics), formaldehyde solution (37-41% w/v, Merck), sodium nitrite (Merck, AR Grade), aniline (Merck, AR Grade), conc. hydrochloric acid (Merck, AR Grade), sodium acetate crystal (Merck, AR Grade), glacial acetic acid (Merck, AR Grade), tetrabutyl ammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>, Aldrich, >99%) where used as received. PCBM was purchased from SolleneBV (purity >99.9%).

## 2.2. Instruments and measurements

$^1\text{H}$  Nuclear magnetic resonance ( $^1\text{HNMR}$ ) spectrum was recorded on a Bruker 400 MHz spectrometer with TMS as internal standard using  $\text{CDCl}_3$  as solvent. FT-IR spectrum of the polymer was taken on a Bruker 550 Spectrometer with spectral range of  $4000\text{-}400\text{ cm}^{-1}$ . Spectra were recorded at a resolution of  $4\text{ cm}^{-1}$  with 32 scans. The polymer sample was finely ground with KBr powder and pressed into pellets. UV-Visible spectra were recorded on Thermo Scientific Evolution 201 UV-Visible spectrophotometer. Fluorescence spectra of the samples were taken using Fluoromax-3 fluorimeter. Thermogravimetric analysis (TG/DTG) was recorded on Q-50, TA instrument at a heating rate of  $20\text{ }^\circ\text{C}/\text{min}$  under nitrogen atmosphere. The CHN analysis was done from Elementar Vario EL III CHNSO elemental analyzer. Gel permeation chromatography (GPC) against polystyrene standards was performed in toluene as eluent on a Waters High Pressure GPC unit with 515 HPLC pump, styragel column and 2414 refractive index detector. A typical concentration of  $0.25\text{ mg}$  of polymer was dissolved in  $5\text{ mL}$  of toluene was used for performing GPC studies. The electrochemical experiments were performed in dry acetonitrile with  $\text{Bu}_4\text{NPF}_6$  as supporting electrolyte using BAS Epsilon Electrochemical analyzer with scan rate of  $100\text{ mV}/\text{s}$ . The steady state photocurrent measurements were done using Keithly-236 Source Measure Unit and Optically pumped semiconductor laser ( $488\text{ nm}$ , Coherent) was used as laser source.

## 2.3. Synthesis methods

### 2.3.1. Synthesis of p-aminoazobenzene (PAZB)

p-aminoazobenzene was synthesized according to the reported procedure (Scheme 1) [29]. Aniline ( $2\text{ g}$ ,  $21.7\text{ mmol}$ ) was added drop wise to a solution of 37% conc. HCl ( $6.5\text{ mL}$ ) and diazotized with an aqueous solution of sodium nitrite ( $1.51\text{ g}$ ,  $21.7\text{ mmol}$ ) at  $0\text{-}5\text{ }^\circ\text{C}$ . The mixture was stirred for 1h. A yellow transparent diazonium salt solution was obtained. The coupling solution was prepared by treating aniline ( $2\text{ g}$ ,  $21.7\text{ mmol}$ ) with hydrochloric acid (1N,  $22\text{ mL}$ ) under vigorous stirring at  $0\text{-}5\text{ }^\circ\text{C}$ . The diazonium salt solution was added drop wise to the coupling solution keeping the temperature at  $0\text{-}5\text{ }^\circ\text{C}$ . The system was kept stirred at  $5\text{ }^\circ\text{C}$  for further 3h. The final solution was added slowly to ammonia solution (1N,  $30\text{ mL}$ ) and a yellow-orange precipitate of azo compound was obtained. The precipitate was filtered and washed several times with water containing a small amount of sodium bicarbonate (pH 8). The precipitate was collected by filtration and washed with deionized water and dried under vacuum. Yellow orange crystal obtained was recrystallized from ethanol.

Yield: 73%; LC-MS ( $M_w\text{-}197$ ,  $M^+$ ). Elemental Analysis: Calculated %: C 73.09; H 5.61; N 21.31. Found (%): C 72.92; H, 5.99; N, 20.98.

### 2.3.2. Synthesis of poly([4-(6-tert-butyl-4H-benzo[e][1,3]oxazin-3-yl)phenyl]-phenyldiazene) (AZO-PBZ).

The synthesis of the polymer is shown in Scheme 2. A mixture of 4-tertiarybutyl phenol ( $10.6\text{ g}$ ,  $70\text{ mmol}$ ) and formaldehyde solution ( $11\text{ mL}$ ,  $175\text{ mmol}$ ) taken in a two necked round bottom flask, were heated to  $40\text{ }^\circ\text{C}$  for 5 h. PAZB ( $13.8\text{ g}$ ,  $80\text{ mmol}$ ) was added slowly to the above mixture. The mixture was stirred at  $180\text{ }^\circ\text{C}$  for 12 h and cooled to room temperature. Dean Stark apparatus was used to collect water as byproduct so as to keep the temperature of the reaction mixture at  $180\text{ }^\circ\text{C}$ . The dark orange solid obtained was dissolved in chloroform and re-precipitated from methanol. The precipitated polymer was filtered, washed with water, dried at

room temperature and further purified by soxhlet extraction with methanol and dried under vacuum. Yield: 83%.

## 2.4. Photoconductivity sample preparation

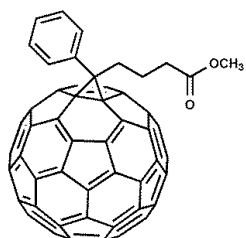


Figure 1 Chemical structure of sensitizer, PCBM

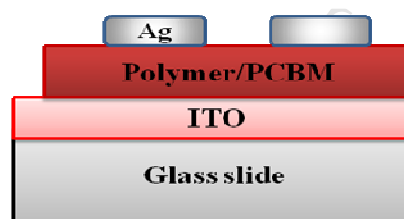


Figure 2 Schematic diagram of sandwich cell structure

Thin films of AZO-PBZ: PCBM blend were prepared from the blend solution in which AZO-PBZ to PCBM (Figure 1) ratio was 1:0.5. The blend solution of polymer and sensitizer was prepared in distilled chloroform by bath sonication method. A clear solution was obtained by filtering the dissolved solution using 0.45 $\mu$ m PTFE filter. To prepare neat films, the clear solution was subsequently spin coated on ITO coated glass substrates. The prepared films had a thickness of 1 $\mu$ m. Conductivity studies were done on sandwich cell structure (Figure 2.) made by vacuum deposition of silver on shadow-masked film samples. The silver electrode has a thickness of 50 nm. The active area of the device (defined by the silver contact) was 0.03 cm<sup>2</sup>.

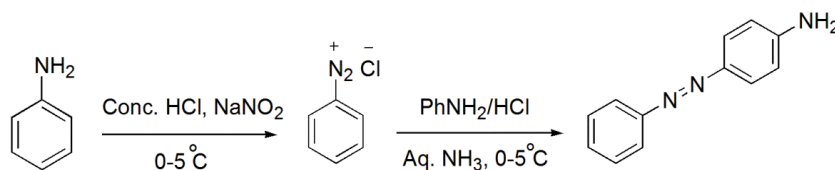
## 2.5. Photocurrent measurement

The steady state photocurrent measurements were done using Keithly 236 Source measure unit. The photocurrent action spectrum was measured using the various excitation wavelengths from a Fluoromax-3 fluorimeter. The photocurrents corresponding to different wavelengths were normalized for constant incident flux. The current through the device prior to illumination (Dark current) was subtracted from current measured under illumination to give the photocurrent ( $J_{PH} = J_L - J_D$ ). Both measurements were done in an air conditioned laboratory maintaining a constant temperature of 25 $\pm$ 0.5 °C. The photoconductivity in polymers depends both on the intensity of illumination and the external electric field and dependence of photocurrent on these parameters were analyzed using the photon flux of wavelength 488 nm.

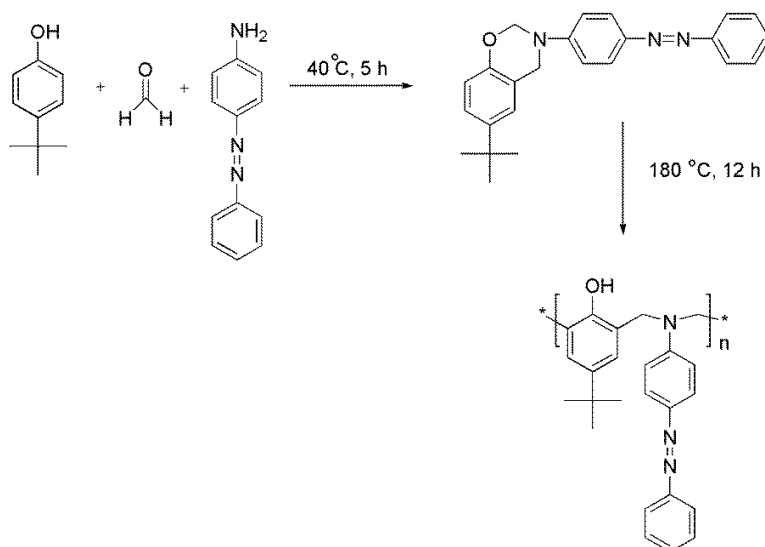
## 3. Results and Discussion

### 3.1. Polymer synthesis

Poly([4-(6-tert-butyl-4H-benzo[e][1,3]oxazin-3-yl)phenyl]-phenyldiazene) was synthesized by thermally activated cationic ring opening polymerization. The reaction was performed in a single step by reacting stoichiometric ratio of tertiarybutyl phenol, p-aminoazobenzene and formaldehyde without using any catalyst and without separating the monomer during the course of reaction.



Scheme 1: Synthesis of p-aminoazobenzene (PAZB)



Scheme 2 : Synthesis of AZO-PBZ

AZO-PBZ has individual electron rich units in its main chain so that it can be treated as a hole transporting agent and aromatic ring having azo group appears as a pendant. Tertiary butyl group present in the 4<sup>th</sup> position of phenol is used to avoid the crosslinking of polymer chains which may reduce the performance of AZO-PBZ towards optical properties. AZO-PBZ polymer was prepared in high yield (83 %) and the monomer p-aminoazobenzene was synthesized by diazotization method according to the literature [29]. AZO-PBZ polymer is soluble in organic solvents like toluene, chloroform, xylene and tetrahydrofuran at room temperature and exhibits good thin film forming properties for device applications. The polymer synthesized in this study is not expected to form high molecular weight because the reactive site of the phenolic moiety has been blocked by bulky tertiary butyl group. Hence, AZO-PBZ is soluble in common organic solvents, makes it possible to record solution state NMR, GPC analysis and absorption studies. The weight average molecular weight ( $M_w$ ) of the polymer was 3124 with a polydispersity index of 1.82. Aniline based polybenzoxazine with low molecular weight was reported earlier [13].

### 3.2. Structural characterization

$^1\text{H}$  NMR spectrum of the polymer is shown in Figure 3. The peak at 1.28 ppm corresponds to methyl protons of the tertiary butyl group. The resonance peak at 4.35 ppm is assigned to methylene units ( $\text{Ar-CH}_2\text{-N}$ ) of oxazine ring Mannich base bridge. Aromatic signals of the tertiary butyl phenol unit and benzene ring attached to azo group appear from 6.72 to 7.93 ppm. The tertiary butyl group present in the phenol moiety and the aromatic protons remain in the polymer chain could confirm the presence of polybenzoxazine unit in the final structure of the polymer.  $^1\text{H}$  NMR analysis clearly indicated that phenoxy structure is completely transformed into phenolic structure by rearrangement. It has been also reported that phenoxy methylene units are highly labile and finally transformed into relatively stable phenolic methylene groups. The signal at 4.35 ppm clearly demonstrates the existence of true phenolic methylene groups [30].



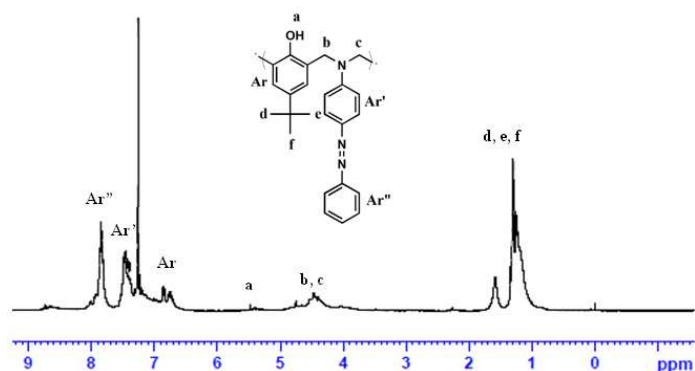
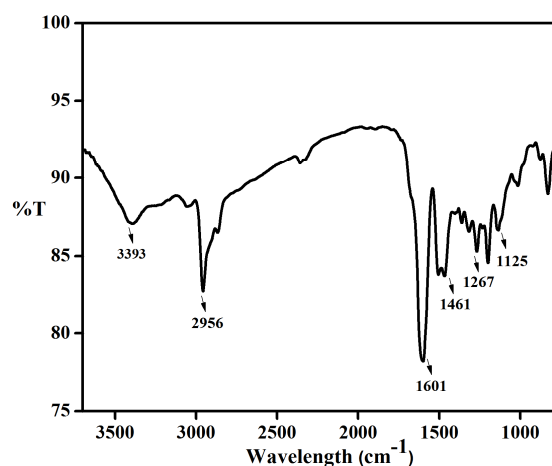
Figure 3.  $^1\text{H}$  NMR spectrum of AZO-PBZ

Figure 4. FT-IR spectrum of AZO-PBZ

The FT-IR spectrum of the corresponding polymer also supported the evidences of the successful achievement of complete ring opening of benzoxazine monomer (Figure 4). Vibrational assignments of various benzoxazine based polymers were reported [30]. The broad peak at  $3393\text{ cm}^{-1}$  could confirm the formation of hydroxyl peak corresponds to the phenolic moiety of the polybenzoxazine chain. The band centered at  $1125\text{ cm}^{-1}$  is assigned to the asymmetric stretching vibration of C-N-C linkage. The stretching vibrations of N=N absorption bands is typically located at  $1461\text{ cm}^{-1}$ . No correlatable band was observed in the region of  $1050\text{-}1010\text{ cm}^{-1}$ , indicating the lack of aliphatic C-O stretching in the polymer which confirms that Mannich phenolic type base bridge present in the repeating unit of the polymer backbone. The presence of a band at  $1267\text{ cm}^{-1}$  is due to aromatic C-O stretching frequency of phenols which is in good agreement with the phenolic type structure of the polymer chain [30].

### 3.3. Thermal Analysis

Thermal stability of AZO-PBZ was studied by TG/DTG curves of the polymer under nitrogen exposure and is shown in Figure 5. The TG/DTG traces of the polymer showed that more than one decomposition events occurred during the thermal degradation of AZO-PBZ. Initial degradation process starting around  $200\text{ }^\circ\text{C}$  and reached its maximum rate of  $0.38\text{ \%}/^\circ\text{C}$  at  $270\text{ }^\circ\text{C}$  due to the cleavage of Mannich base [31] which is the consequence of evaporation of amine. The second weight loss corresponding to the degradation of phenol moieties appeared at  $360\text{ }^\circ\text{C}$  with a maximum rate of  $0.07\text{ \%}/^\circ\text{C}$  at  $405\text{ }^\circ\text{C}$ . These peaks attributed to primary decomposition products involve the cleavage of C-N and C-O linkages [18,31] present in the polymer structure. The peak appeared above  $450\text{ }^\circ\text{C}$  is associated with secondary decomposition products due to the functionalities which are not incorporate in to the polymer chain [18]. From the figure it is seen that AZO-PBZ was fairly stable up to  $200\text{ }^\circ\text{C}$ . This could be due to the amine evaporation and Mannich base cleavage of the polymer backbone [27].



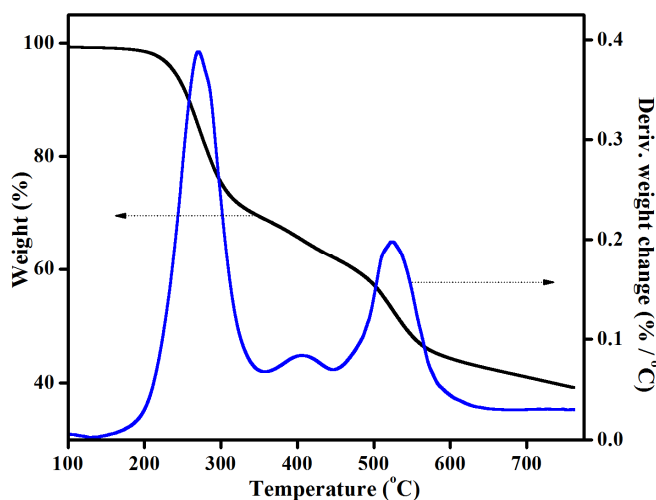


Figure 5 TG/DTG plot of AZO-PBZ

### 3.4. Photophysical properties

The UV-Vis absorption spectra of AZO-PBZ in solution and as thin film which was prepared on ITO coated glass substrates are shown in Figure 6. The band below 350 nm corresponds to  $\pi - \pi^*$  transition of the aromatic ring present in the structure of the polymer. The polymer backbone has electron rich *t*-butyl substituted phenyl ring which acts as a donor and *p*-aminoazobenzene acts as an electron acceptor. The peak at higher wavelength region is attributed to the formation of intramolecular charge transfer complex. The optical edge of the polymer in solution was at 506 nm from which the optical band gap ( $E_g^{Opt}$ ) was calculated to be 2.45 eV. The absorption onset of the polymer film is at 555 nm, corresponding to an optical band gap of 2.23 eV so that AZO-PBZ can be loosely defined as a narrow band gap polymer [32], which corresponds to the combined contribution of  $n-\pi^*$  and intramolecular charge transfer electronic transition of azobenzene chromospheres. The absorption spectrum of the polymer in film form appeared slightly red shifted as a result of interchain interactions in the solid film [33].

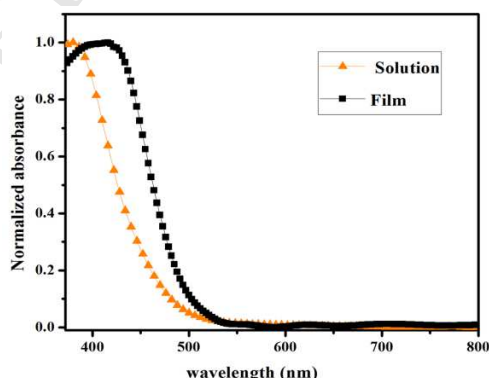


Figure 6 Absorption spectra of (a) AZO-PBZ dissolved in chloroform and (b) AZO-PBZ as thin films on ITO coated glass plate.

When the polymer was blended with the sensitizer PCBM, the absorption spectrum of the blended film exhibited a red shift compared to that of pristine film. The incorporation of sensitizer PCBM with AZO-PBZ resulted in a significant enhancement in the absorption coefficient (Figure 7) of the blend film. The absorption spectrum of the PCBM thin film is also shown the inset of Figure 7. The optical absorption spectrum of the AZO-PBZ:PCBM blend films could be considered as the simple superposition of the absorption spectra of these two components. There is no indication of the substantial interaction between the polymer and sensitizer in its ground state. This can be confirmed by measuring the dark electrical conductivity of the pristine and blend films. Both the samples possess the same value of electrical conductivity which confirms this statement. Thus, the AZO-PBZ:PCBM blend films form a neutral electron donor-acceptor complex in which the overlapping of the electronic wave function in the ground state is negligible.

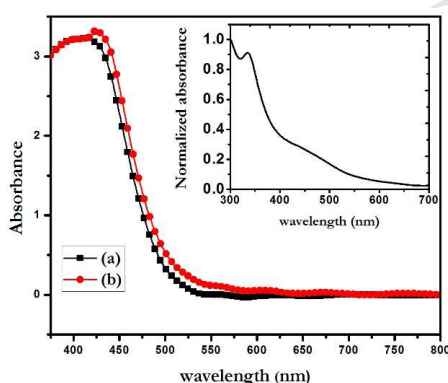


Figure 7 Absorption spectra of (a) pristine AZO-PBZ thin film and (b) AZO-PBZ:PCBM blend film (1:0.5). Inset shows the absorption spectrum of PCBM thin film. All films were prepared on ITO coated glass plate.

### 3.5. Fluorescence quenching

The fluorescence spectrum of the AZO-PBZ was studied, by exciting with photons of wavelength 380 nm, in solution and in film, with and without adding PCBM. The fluorescence spectra of AZO-PBZ dissolved in chloroform and as thin film prepared on ITO coated glass substrates are shown in Figure 8. The emission maximum occurs at 597 nm. Incorporation of PCBM molecules leads to a drastic quenching of the fluorescent intensity of the blend films (figure 9).

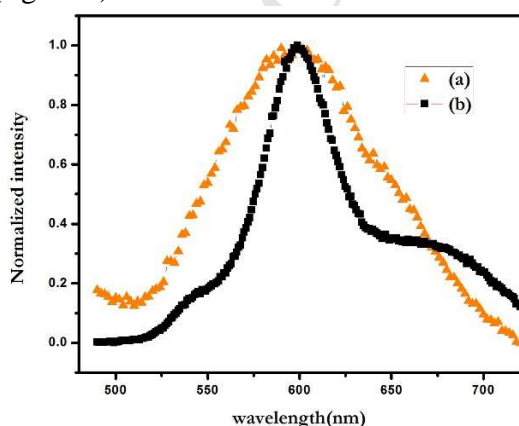


Figure 8 Fluorescence spectra of (a) AZO-PBZ dissolved in chloroform and (b) AZO-PBZ thin film prepared on ITO coated glass plates

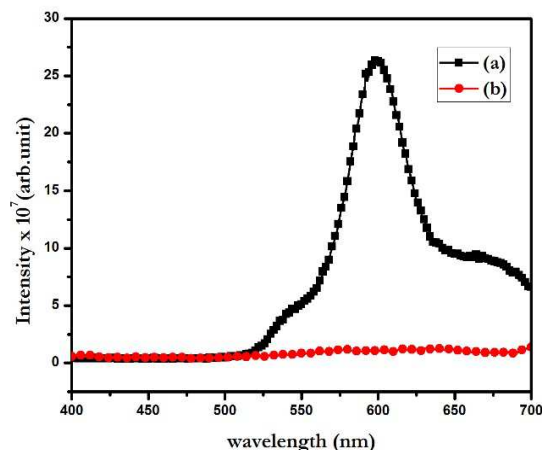


Figure 9 Fluorescence spectra of (a) AZO-PBZ thin film and (b) AZO-PBZ:PCBM blend films for the ratio 1:0.5

The absorption onset of PCBM in solid state is at 425 nm [34]. There is no significant overlap between the emission band of AZO-PBZ and absorption band of PCBM which ruled out the possibility of energy transfer process leading to the quenching of the fluorescence intensity [19,35]. AZO-PBZ:PCBM blend films exhibited enhanced conductivity during irradiation. So the quenching of the fluorescence intensity can be attributed to the photoinduced intermolecular charge transfer of electrons from AZO-PBZ to the sensitizer, PCBM. The AZO-PBZ:PCBM blend films therefore can be of much use in photoconductive applications.

### 3.6. Electrochemical properties

Electrochemical properties of AZO-PBZ were investigated using cyclic voltammetry. CV was performed at 25 °C in a solution of Bu<sub>4</sub>NPF<sub>6</sub> (0.1M) in dry acetonitrile at 100 mV/s under nitrogen atmosphere. The experimental set up includes a three electrode configuration with Ag/AgCl reference electrode, a platinum working electrode (0.08 cm<sup>2</sup>) coated with the thin polymer film and a platinum wire as counter electrode. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the AZO-PBZ polymer can be estimated from the onset of oxidation ( $E_{onset}^{ox}$ ) and reduction ( $E_{onset}^{red}$ ) potentials [36]. From the value of ( $E_{onset}^{ox}$ ) and ( $E_{onset}^{red}$ ), the HOMO and LUMO as well as the electrochemical band gap ( $E_g$ ) of the polymer were calculated by the following equation [37].

$$\text{HOMO} = - (E_{onset}^{ox} + 4.71) \text{ eV} \text{ ----- (1)}$$

$$\text{LUMO} = - (E_{onset}^{red} + 4.71) \text{ eV} \text{ ----- (2)}$$

$$E_g = (E_{onset}^{ox} - E_{onset}^{red}) \text{ eV} \text{ ----- (3)}$$

The onset of oxidation of AZO-PBZ was found to occur at 0.88 V corresponding to ionization potential value of -5.58 eV. HOMO and LUMO levels of the polymer obtained from the electrochemical measurement were -5.58 eV and -3.56 eV respectively. Therefore, band gap of the polymer is calculated to be 2.20 eV which is a lower value than that of the optical energy gap (2.45 eV) obtained from absorption onset. The incorporation of azo group increases a slight increase of HOMO level, may be due to the contribution of electron rich units in its structure. AZO-PBZ exhibited an optical band gap of 2.45 eV much lower than poly(vinylcarbazole) (4.10 eV), a well known photoconductor [38].

### 3.7. Steady state photocurrent measurement

The spectral dependence of the steady state photocurrent was measured as explained in the experimental section. AZO-PBZ sandwich cell was found to be a poor conductor of electricity in its intrinsic state and the observed dark current was much low. The incorporation of PCBM molecules resulted in a considerable increase in the optical absorption which leads to a noticeable change in the photocurrent through the sample. This increase in photocurrent in the blend films indicates the effective photosensitization, increase in quantum efficiency of the charge carriers and its transport through the films.

The photocurrent action spectrum was recorded for the blend films in which AZO-PBZ to PCBM ratio was 1:0.5, by irradiating with photons of wavelength from 300 nm (4.14 eV) to 700 nm (1.77 eV) at an applied electric field of 10V/μm. The action spectrum measured for both the

positive and negative polarities of ITO, is shown in Figure 10. When the ITO electrode is negatively biased, the AZO-PBZ:PCBM films exhibited an enhanced photocurrent over the entire spectral range.

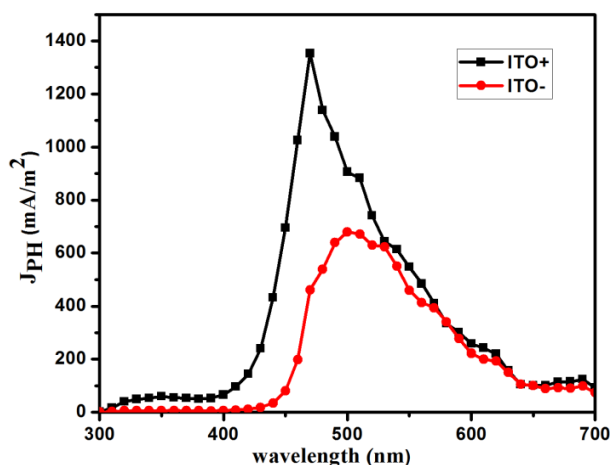


Figure 10 Action spectra of AZO-PBZ:PCBM blend films for the polymer to PCBM ratio 1: 0.5 for different polarities of ITO at 10 V/μm

The onset of action spectrum is at 1.90 eV (653 nm). Photocurrent increases with photon energies and a maximum photoresponse was obtained for 2.66 eV (470 nm). For photons with energy greater than 2.66 eV, photocurrent was found to be decreasing. The photocurrent gradually decreased for energy greater than 3 eV (414 nm). The maximum spectral response was obtained at the onset of the optical absorption of the pristine AZO-PBZ film. The blend films exhibited an increase in photocurrent at 430 nm, which corresponded to the onset of absorption of PCBM thin film.

The dependence of photocurrent on intensity of illumination was studied using a laser beam of wavelength 488 nm by applying an electric field of 10 V/μm (Figure 11). The intensity of the laser beam was varied using a polarizer. The power law dependence of the photocurrent on the intensity of the incident light beam was found to be slightly sub linear;  $J_{PH} \propto I^{0.87}$ , and it is the general behavior of most of the amorphous semiconducting materials [39,40].

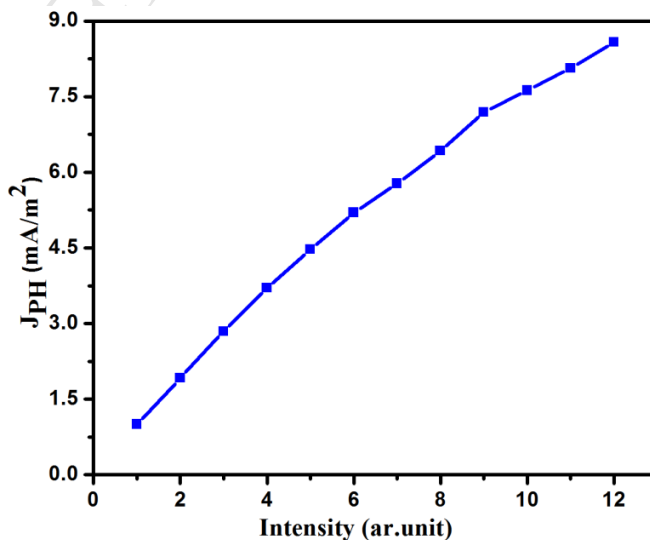


Figure 11 Intensity dependence of photocurrent of AZO-PBZ:PCBM blend films with polymer to PCBM ratio 1:0.5 by irradiating with laser beam of wavelength 488 nm at an applied electric field of 10 V/μm

The photogeneration efficiency and photoconductive sensitivity of the PCBM blend films were calculated as a function of the electric field by measuring the photocurrent through the sample.

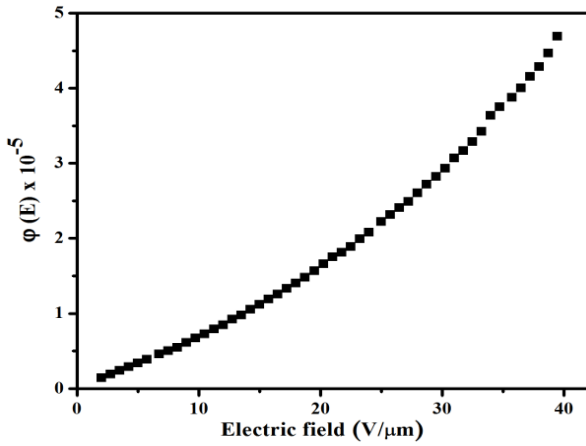


Figure 12 Electric field dependence of internal photogeneration efficiency of AZO-PBZ:PCBM blend films with polymer to PCBM ratio 1:0.5 by irradiating with laser beam of wavelength 488 nm with intensity of 125 mW/cm<sup>2</sup>

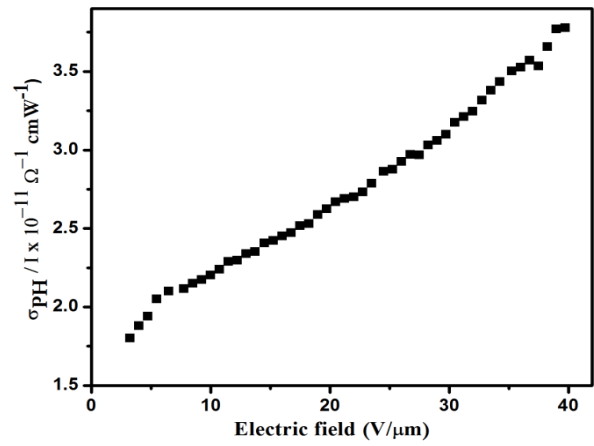


Figure 13 Electric field dependence of photoconductive sensitivity of AZO-PBZ:PCBM blend films with polymer to PCBM ratio 1:0.5 by irradiating with laser beam of wavelength 488 nm with intensity of 125 mW/cm<sup>2</sup>

Photogeneration efficiency ( $\phi$ ) is defined as the number of measured charge carriers per absorbed photon [41], which is calculated using the expression,

$$\phi = \frac{hc}{e\lambda \ln \alpha L} \frac{I_{ph}}{I} \quad \text{-----} \quad (4)$$

where,  $I$  is the light intensity,  $L$  is the thickness of the sample,  $\alpha$  is the absorption coefficient and  $\lambda$  is the wavelength of light used. Photoconductive sensitivity is defined as the photoconductivity per unit light intensity and was calculated using the equation,

$$\frac{\sigma_{ph}}{I} = \frac{I_{ph} L}{IV} \quad \text{-----} \quad (5)$$

where,  $V$  is the applied voltage. The photocurrent measurements were carried out on PCBM

blend thin films by varying the electric field through the samples at an illumination intensity of 125 mWcm<sup>-2</sup>. The samples can withstand electric fields upto 40 V/μm and beyond this the samples undergo dielectric breakdown. Photoconductive sensitivity and photogeneration efficiency were calculated and is plotted as function of the electric field (Figure. 12 and Figure. 13). It is observed that, at low electric fields, the photocurrent and the photogeneration efficiency exhibited a linear power law dependence with the electric field and at higher electric fields it is super linear ( $E^{1.7}$ ). This strong dependence of photogeneration on the electric field suggests the

relevance of Onsager's theory of geminate ion pair dissociation [42,43]. The calculated values of the photoconductive sensitivity are of the order of 10<sup>-11</sup> and photogeneration efficiency is of the order of 10<sup>-5</sup>.

#### 4. Conclusions

P-aminoazobenzene based non-conjugated benzoxazine polymer, Poly([4-(6-tert-butyl-4*H*-benzo[e][1,3]oxazin-3-yl)phenyl]-phenyldiazene) (AZO-PBZ) was successfully synthesized by solventless, thermally activated cationic ring opening polymerization. The steady state photocurrent measurements revealed that, this low band gap polymer when blended with PCBM, exhibited good photoresponse over the entire spectral range. Both internal photocurrent efficiency and photoconductive sensitivity strongly depend on the external electric field. Internal photocurrent efficiency of the blend film is of the order of  $10^{-5}$  and photoconductive sensitivity is of the order of  $10^{-11}$  S W<sup>-1</sup>cm. These values are promising when a photorefractive material is concerned and for the fulfilment of such materials. The other important parameter electro-optic co-efficient has to be considered which is in progress.

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## Highlights

- **Photoconducting, non conjugated p-aminoazobenzene based polybenzoxazine was synthesized successfully via solventless, cationic ring opening polymerization.**
- **Polymer was characterized by optical and electrochemical methods.**
- **The dependence of photocurrent on intensity of illumination and applied electric field was investigated.**
- **Achieved good internal photocurrent efficiency and photoconductive sensitivity in AZO-PBZ: PCBM blend.**