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Effect of Heterocyclic Compound on Synthesis and Characterization of New Organic Material used for Photovoltaics

Ravindra Kumar Singh¹ & Pradeep Kumar²

¹Research Scholar, Department of Chemistry, Shri Venkateshwara University, Gajraula, Amroha, India.

²Department of Chemistry, Shri Venkateshwara University, Gajraula, Amroha, India.

ABSTRACT - The organic molecules is also be made through chemical reactions that do not involve life. The basic structures of the organic molecules are produced from various lipids, carbohydrates and proteins as well as tannin, cutin, and lignin. A conjugate organic material also called polymer is a large molecule, which is composed of many repeated subunits of carbon and other molecules. Because of showing, its large range of applications and properties, both synthetic and natural polymers play an essential role in daily life. The organic photovoltaics are notv made of semiconductor p-n junctions but it is synthesized from electron donor and electron acceptor materials. The molecules forming the electron donor region of organic photovoltaic, where excitons electron-hole pairs are produced, are generally conjugated organic polymers, which posses delocalized π electrons and resulting hybridization by carbon p orbital. The π electrons may be excited by the visible part of the spectrum light, so that it may move from the molecule's highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), denoted by a π - π^* transition. The research work objective is to find out the new organic material, which may show photovoltaic properties and use for photovoltaic applications. For this objective the fluorescence quenching studies were done with varying ratios of PCBM. It was observed that the fluorescence intensity of P_x new organic material decreased gradually with increase in weight ratio of PCBM. This has indicated that there is an electron transfer from P_x to PCBM resulting into fluorescence quenching, which show the properties of photovoltaic applications.

Key words: Heterocyclic Compound, photovoltaic, bulk heterojunction polymer, nucleophilic Substitution, new organic material, synthesis, characterization.

I. Introduction

The organic material introduces to the large chain of carbon-based compounds. It is found within terrestrial and aquatic environments, natural and engineered. It is the matter, which composed of organic compounds, produced from the animal's and plant's remains of organisms and their waste products already present in the environment. The organic molecules is also be made through chemical reactions that donot involve life [1]. The basic structures of the organic molecules are produced from various lipids, carbohydrates and proteins as well as tannin, cutin, and lignin.[2]. Organic material plays a very important role in the movement of nutrients for the environment and for water retention on planet's surfaces [3]. A conjugate organic material also called polymer is a large molecule, which is composed of many repeated subunits of carbon and other molecules. Because of showing, its large range of applications and properties, [4] both synthetic and natural polymers play an essential role in daily life [5]. India has abundant sources of power production. This is currently generated by State utilities, and the Central utilities and Private players. Indian power sector is evolving from the "nascent opening" market phase to a developing phase [6].

The organic Polymers are widely used as the material to synthesize the solar cell which is used in photovoltaic applications. The photovoltaic is a type of flexible solar cell, which is made with large molecules with repeating structural units, polymers, which produce electric energy from sunlight by the photovoltaic effect. The polymer solar cells consist of organic solar cells. They are special types of thin films, while others are having the more stable silicon solar cell. In comparison to silicon material based devices, the solar cells are inexpensive to fabricate, potentially disposable, lightweight, and, flexible, potentially have less adverse environmental impact customizable on the molecular level.

The organic solar cells inefficiency and stability problems, [7] combined with their promise of less costing [8] and increased efficiency [9] made them a popular field in solar cell research. As of 2015, polymer solar cells were able to achieve over 11% efficiency via a tandem structure. [10] In bulk heterojunction polymer solar cells, light generates excitons. The ionic charges separation between an electron donor and acceptor and mixed within the active layer of the device's. The charges then transported to the electrodes of the device, where the charges flow from the cell, perform work and then re-enter the device in the opposite side of the device. The efficiency of the cell is limited to several factors. The hole mobility gives to faster conduction across the active layer [11, 12]. The organic photovoltaic is synthesized of electron donor and electron acceptor materials. The organic molecules forming the electron donor region of organic photovoltaic, where excitons electron-hole pairs are generated, are generally conjugated organic materials, which possess delocalized π electrons and resulting from hybridization of carbon p orbital. The π electrons may be excited by the visible part of the spectrum light, so that it may move from the molecule's highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), denoted by a π - π^* transition. [13, 14] The energy bandgap between these orbital determines which wavelength of light can be absorbed by the material. Therefore the requirement is to find out such organic material which must be helpful and show photovoltaic properties. The heterocyclic such as triazoles are observed to have a unique π - structure assisted by charge transfer electronic structure. However, their optical and electrical properties are not desirable. Also, it has not been studied the effect of attachment of heteroaromatic cycle to the direct attachment to thiophene backbone on each repeating unit.

II. Experimental Details

All chemicals were purchased from commercial sources (Aldrich) and used without further purification, unless otherwise noted. THF was distilled from sodium-benzophenoneketyl. NBS was recrystallized from water. The monitoring of reactions was carried out on glass-supported silica gel coated with fluorescent indicator F254. *The flash chromatography was performed using silica gel from chromatography technologies.* All ^1H and ^{13}C $\{^1\text{H}\}$ NMR spectrum were recorded on a high resolution NMR spectrometer. Chemical shifts and coupling constants are reported in parts per million and Hz, respectively. For UV-vis absorption spectrum, stock solutions of polymers ($c=1\text{mg}/10\text{mL}$) were prepared in spectrophotometric grade chloroform (Fisher). UV-vis experiments for thin films were done by spin casting (1400 rpm) of 1 wt % solution of polymer in chloroform on a glass plate. Similarly, to the 1 wt % solution of polymer in chloroform PCBM was added and spins casted onto a glass plate. These films were annealed at 105°C for 35 minutes; UV-Vis and Fluorescence spectrum were measured before and after doing annealing process. Fluorescence spectrums were measured on PTA flourimeter for thin films & on FLS 980 spectro fluorometer for solutions studies. Cyclic Voltammeter studies were done using BAS CV-50 W instrument. The solutions of polymer were prepared & films are spin casted on the platinum working electrode was recorded with tetrabutylammonium hexfluorophosphate as a supporting electrolyte in acetonitrile. The redox potentials were determined versus an Ag/Ag^+ reference electrode.

III. Process to Synthesize New Organic Material

The synthesis of the new organic material from 3-bromothiophene, which converted to 3-iodothiophene (a) using the nucleophilic Substitution [15]. The compound (a) was dibrominated using N-bromosuccinimide followed by the coupling with trimethylsilylacetylene and 1,3-dipolar cyclo addition with 1-azidohexane gave new organic polymer (Figure 2.1) in the form of good product.

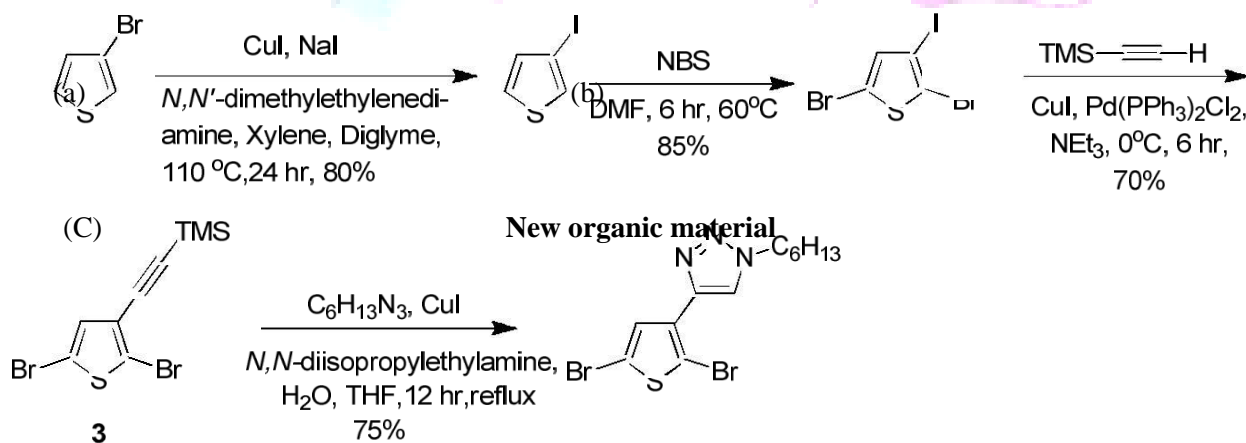
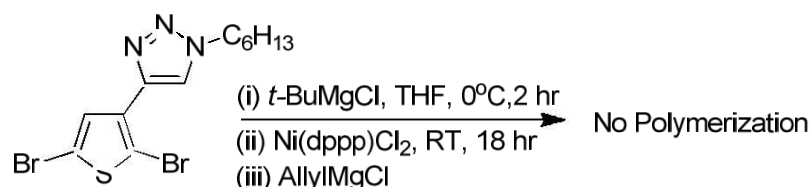


Fig 3.1 Synthesis technique for new organic material

The fabrication is done for new organic polymer to synthesize the polymer using standard Ni (0)-mediated [16] Grignard reaction. When the reaction mixture was poured into methanol; no precipitate was obtained, indicating the absence of polymeric products. We did not obtain a precipitate irrespective of

whether the polymerization was done at room temperature or at elevated temperatures for 24 h. We hypothesized that the failure of the polymerization may be either due to the inability of new organic polymer to undergo Grignard metathesis, So to overcome this problem, it is decided to design an alternate technique to synthesize the new material which will produce new organic polymer P_3T_2T (P_x) and also it is necessary to understand why this new organic polymer (Figure 2.2) does not produce polymeric products.



New organic polymer

Fig 3.2- Synthesis techniques for polymerization from new organic polymer (P_1)

IV. Quenching Studies of New Organic Polymer

It is concluded to do quenching studies, as new organic polymer (P_1) does not produce polymeric products using Grignard reaction. In which, this polymer was reacted with *t*-BuMgCl for 1.5h and the reaction mixture was quenched with water. The organic components were extracted with diethyl ether, and the solvent was removed under reduced pressure. The NMR of residue showed presence of regioisomers. NMR results have shown that Grignard reaction occurred with Br group at second position which is *ortho* to triazole moiety. The reason of formation of Grignard at this position could be due to the coordination of triazole nitrogen and acting chelating agent for Mg^{2+} . Therefore, a new organic polymer (P_2) for polymer (P_x) using almost same protocol with some modification in synthesis route synthesized. It is started from readily available 3-bromothiophene which was converted to 3-iodothiophene (a) using the nucleophilic substitution process. The compound was mono-brominated using (a) equivalence of *N*-bromosuccinimide followed by the coupling with trimethylsilylacetylene and 1,3-dipolar cycloaddition with 1-azidohexaneproduced new material P2 in good products. It is passed thorough variety of iodination conditions and found that *N*-iodosuccinimide and trifluoromethanesulfonic acid (NIS/ CF_3SO_3H) provided the iodinated compound in excellent product. P2 was reacted with *t*-BuMgCl, and the reaction mixture was quenched with water. NMR studies have shown that Grignard metathesis happening at the fifth position. It was concluded to note that P2 was polymerized (fig-4.1) under Grignard reagent conditions [15].

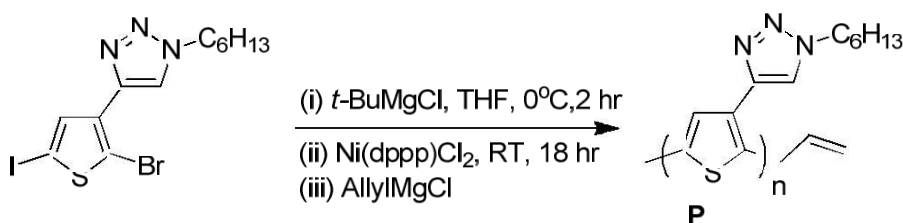


Fig-4.1 Polymer (P_x) synthesis from new organic polymer (P_2)

V. Characterization of new organic material

From the available theories, it is evident that heterocyclic (1,2,3-triazole) can act as an electron donor or as an electron acceptor [17]. If triazole acts as electron donor, then it is expected that the homo levels of the polymer will be affected and if it acts as an acceptor the lumo level of a conjugated polymer will get affected, [18] which is a very important part of any photovoltaic. The resonance and inductive effects of triazole will also depend on the orientation of the triazole ring with respect to the backbone. Therefore, it is very importance to understand the impact of triazole on the electronic structure of the conjugated polymer backbone and on the frontier energy levels. In characterization of the organic material, the UV-vis absorption of the polymer was studied in solution as well as thin films. Solution state UV was found using a solution of polymer in chloroform and solid state measurements were done by casting a thin film of polymer from same solution and spectrum were recorded before and after thermal annealing at 100°C for 30 min. The absorption in solution is 414 nm and in thin film is 503 nm with a red shift of 90 nm in thin films. In comparison, P3HT has a red shift of 115 nm in thin films. To find out that the polymer P_x is a compound for organic photovoltaic applications, fluorescence quenching studies were done with varying ratios of PCBM. It was observed that the fluorescence intensity of P_x polymer decreased gradually with increase in weight ratio of PCBM. This has indicated that there is an electron transfer from P_x to PCBM resulting into fluorescence quenching. Thin film of 1:1 wt% P_x and PCBM was casted onto a glass plate did not show any fluorescence indicating complete fluorescence quenching of a polymer. Therefore, as the properties of new organic material are found matched with PCBM so the work concluded that P_x is an organic material which can also be used for organic photovoltaic applications. In NMR spectrum of new organic material P₂ (fig-5.1), there are 3 protons in a romatic region 1 from triazole (8.17 ppm) and other two were from thiophene proton (7.62 ppm and 7.3 ppm respectively). Triplet at 4.35 ppm corresponds to -CH₂ next to nitrogen attached to triazole ring and all other protons of alkyl chain fall in region of 0.85-1.95 ppm. The NMR for P₂ indicates pure compound where in 2 protons in aromatic region corresponds to thiophene proton (7.8 ppm) and triazole proton (8.1 ppm). There is a triplet at 4.35-4.4 ppm corresponding to -CH₂ next to nitrogen of triazole unit.

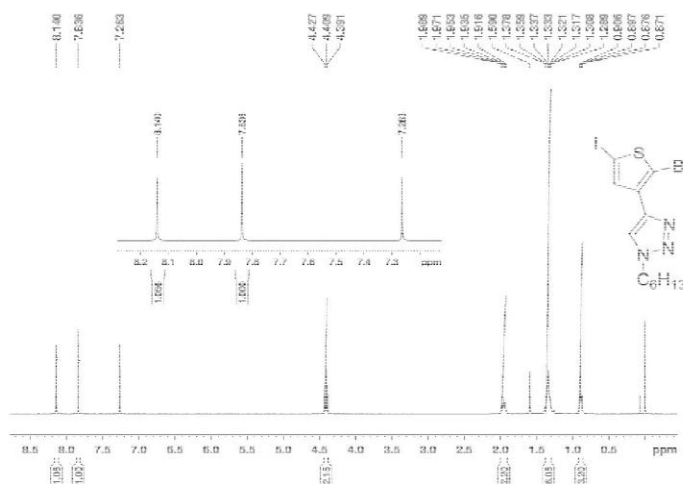


Fig 5.1- NMR of new organic polymer (P₂)

VI. Result and Discussion

The synthesis of new organic material P₁ and P₂ for polymer P_x was complicated. The organic polymer P₁ did not go under polymerization due to formation of Grignard at 2nd position instead of 5th position on thiophene backbone of P₁. The reason of formation of Grignard at this position could be due to the coordination of triazole nitrogen and new organic polymer acting chelating agent for Mg²⁺. It has been identified that CuSO₄/Sodium ascorbate method gives pure products as compared to CuI/DIPEA method for reactions and also CuSO₄/Sodium ascorbate route deletes the possibility of isomers during the reaction. It has been shown that P_x polymer can be synthesized using modified P₂ in which triazole attached as a pendant group and polymerization can be done using Ni (0)-mediated Grignard reaction polymerization. Fluorescence quenching of this polymer with PCBM indicates that it is a useful material for organic photovoltaic devices. The ongoing future work will be evaluating the hole mobilities and photovoltaic of thiophene-based polymers with pendant triazole moiety with different kind of acceptors and new conjugated polymers. Therefore due to the properties of lumo and homo this new organic material shows photovoltaic properties and may be used for photovoltaic applications.

VII. Acknowledgement

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