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Synthesis and optoelectronic properties of dodecyl substituted diphenylamine and pyridine based conjugated molecule

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Abstract. The new donor-acceptor type conjugated moiety, namely 3-([4-(2-Cyano-2pyridine-2yl-vinyl)-phenyl]-dodecyl-amino)-phenyl)-2-pyridine-2-yl-acrylonitrile (**DPA-PA**) has been synthesized according to the Knoevenagel condensation. Here dodecyloxy diphenylamine moiety acts as an electron donor and cyano-pyridyl moiety acts as an electron acceptor. These moieties are recently showing great interest in optoelectronic applications. The structure of the DPA-PA was confirmed by FT-IR, ^{1}H NMR. The final product showed great solubility in common organic solvents such as toluene, tetrahydrofuran, ethyl acetate, dichloromethane, chloroform etc due to the dodecyl chain. The absorption maximum of DPA-PA appeared at 433 nm in chloroform solution. The optical band gap is 2.2 eV calculated from thin film absorption edge (550 nm). The photoluminescence spectra exhibited a maximum peak at 513 nm with greenish fluorescence in chloroform solution and at 541 nm as the thin film state. The emission spectra of thin film state are 28 nm red shifted with broadening peak. The lower electrochemical band gap 1.55 eV was observed by cyclic voltammetry. This type of low band gap materials has much attention for their various potential applications in optoelectronic devices.

1. Introduction

Over last 10 years, very low band gap donor-acceptor based conjugated small molecules are designed and synthesized to focus intense research for various applications. Compared of conjugated small molecules, oligomers and long chain polymers are having some difficulties such as purity and poly-dispersity. So it is required to give more interest for smaller systems of organic molecules, which possess clear chemical characteristic and spectroscopic data. The general attention of the conjugated small molecules is due to their electrochemical, optical, morphological and electrical properties [1,2]. These conjugated small molecule materials may be used in various optoelectronic devices such as organic light-emitting diodes (OLEDs) [3,4] organic thin film transistors (OTFTs) [5] and organic solar cells organic photovoltaic devices (OPVs) [6].

In the donor-acceptor conjugated system, we selected diphenylamine (DPA) as electron donor because of high electron mobility, thermal and photochemical stability. So commonly used as light-emitting materials. The previous literature proved that triphenylamine and diphenylamine derivatives

are good candidates for photovoltaics because of their multifunctional properties, such as most soluble in organic solvents, two-photon absorption, hole-conducting properties, and electrochemical stability, electron donating ability and optoelectronic properties. The rigid and non-planar structure of DPA increases the solubility [7,8].

Electron transfer is the main role in the chemistry and also biology [9]. Many conjugated systems that carry aromatic heterocyclic rings. This helps to increase the hyper polarizability because of the delocalization energy of hetero-aromatics. The Nonlinear optical (NLO) properties are increased due to electron-donor units along the main conjugated chain [10]. Therefore, the diphenylamine moiety should be connected with strong electron-acceptor for decreasing of the electrochemical band gap.

A pyridine ring is an electron deficient molecule and it is highly electron-withdrawing moiety. If it is introduced in the conjugated system, it exhibits good electron-transporting abilities and also optical properties. The low laying lowest unoccupied molecular orbital (LUMO) reduces the environmental oxidation of the molecule, leading to a stable conjugated system. Along with pyridine ring cyano group, it helps to reduce the both highest occupied molecular orbital (HOMO) and LUMO energy level because of its withdrawing nature [11-13].

The current article deals with the synthesis and optoelectronic properties of low band gap diphenylamine-pyridyl acetonitrile (DPA-PA) based conjugated molecule. In this conjugated system, electron-donating diphenylamine moiety was connected with electron withdrawing cyano-pyridyl ring through Knoevenagel condensation. In this conjugated small molecules, donor and acceptor were linked directly with ethylene linkages. These ethylene linkages increase the flexibility, energy levels, increases the solubility, the planarity of the π-conjugated system and also tuning optoelectronic properties [14]. Moreover, we investigated the electrochemical and optical studies of the conjugated molecules.

2. Experimental procedure

2.1. Reagents and solvents

Diphenylamine, Dodecyl bromide, Phosphoryl chloride, 2-Acetonitrile pyridine, Piperidine, Sodium hydride, was purchased from sigma Aldrich, Bangalore, India. Solvents such as DMF Ethyl acetate, DCM, Toluene, respectively were purchased from Sd-fine chemicals, India. All solvents were dried and distilled before the synthesis as per standard methods.

2.2. Characterization methods

FT-IR analysis was recorded on Thermo Nicolet 330 FT-IR spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker Advanced III 400 MHz spectrometer. The UV-visible absorption spectra were recorded on Hitachi U2910 spectra-photometer. The fluorescence emissions were performed with Perkin-Elmer LS45 fluorescence spectrometer. The cyclic voltammogram peaks were recorded on CH-I 660C instrument.

2.3. Synthetic procedure

2.3.1. *Synthesis of dodecyl diphenylamine (2)*. Sodium hydride (0.0059 mol) was added to the solution of diphenylamine (0.0059 mol) in DMF (10 ml). This mixture was stirred for approximately 15 min. After 1-bromo dodecane (0.0059 mol) was slowly added to the reaction mixture and the mixture was stirred for 5 hr at 70 $^{\circ}$C temperature. After completion of the reaction, the mixture was diluted with water and extracted with ethyl acetate and dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography using ethyl acetate and hexane as a mobile phase. ^{1}H NMR (400 MHz, $CDCl_3$, δppm): 7.04 (m, 4H, aromatic ^{1}H), 6.58 (m, 2H, aromatic ^{1}H), 6.43 (m, 4H, aromatic ^{1}H) 3.06 (t, 2H, -N-CH$_2$-), 1.52-0.96 (m, 22H, -CH$_2$ and –CH$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, δppm): 143.2, 129.4, 118, 117.9 (aromatic C), 58.4, 29.2, 23.1, 14.0 (dodecyl chin chain C).

2.3.2. *Synthesis of dicorbaxaldehyde dodecyl diphenylamine (3).* The phosphorus oxychloride (0.3555 mol) was added dropwise to DMF (0.3555 mol) at 0 ^{o}C over a period of 20 min. Then alkylated diphenylamine (2) (0.0237 mol) was added to the above solution and stirred at 90°C for 20 hr. After completion of the reaction, the solution was cooled to room temperature, poured into ice-water, neutralized to pH 6-7 by the dropwise addition of sodium hydroxide solution. The product was extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate. Then crude product was purified by column chromatography using ethyl acetate and hexane as eluent. A light-green color solid was obtained. ^{1}H NMR (400 MHz, CDCl$_3$, δppm): 9.81(s, 2H, aldehyde H), 7.81(d, 4H, aromatic H), 7.13 (d, 4H, aromatic H), 3.83(t, 2H, N-CH$_2$), 1.71(m, 2H, N-CH$_2$CH$_2$_), 1.44-1.28(m, 19H, -CH$_2$), 0.88 (t, 3H, CH$_3$).

2.3.3. *Synthesis of Diphenylamine - Pyridyl acetonitrile based molecule (DPA-PA).* Compound 3 (0.0006 mol) was dissolved in 10 ml of toluene. To this 2- Acetonitrile pyridine (0.0013 mol) was added dropwise at room temperature. Then piperidine (0.0013 mol) was added and the reaction mixture was stirred approximately at 120°C for 2 hr. After completion of the reaction, the mixture was diluted with water extracted with DCM. The crude product was purified by column chromatography using ethyl acetate and hexane as a mobile phase. ^{1}H NMR (400 MHz, CDCl$_3$, δppm): 8.48 (d, 2H, pyridyl CH$_2$), 8.26 (s, 2H, cyano-vinylene H), 7.86 (d, 4H, diphenylamine H), 7.59 (m, 4H, pyridine H), 7.09 (m, 2H, pyridine H), 7.02 (d, 4H, diphenylamine H), 3.69 (t, 2H, N-CH$_2$), 1.59 (m, 2H, N-CH$_2$CH$_2$_), 1.55-1.20 (m, 19H, -CH$_2$), 1.1 (t, 3H, CH$_3$).

3. Result and discussion

3.1. Characterization of donor and DPA-PA

The general synthetic scheme for dicorboxaldehyde diphenylamine (3) and final molecule (DPA-PA) was shown in **scheme 1**. The structure of the intermediate and final product was confirmed by FT-IR, ^{1}H & ^{13}C NMR. Firstly, the dicarboxaldehyde diphenylamine donor was synthesized from compound 2 in presence of DMF and POCl$_3$ through previous literature [8]. The newly formed aldehyde protons appeared at 1678 cm^{-1} in FT-IR, 9.87, 190.4 ppm was appeared in ^{1}H & ^{13}C NMR, which confirms the newly formed aldehyde protons.

Synthesis of donor moiety:
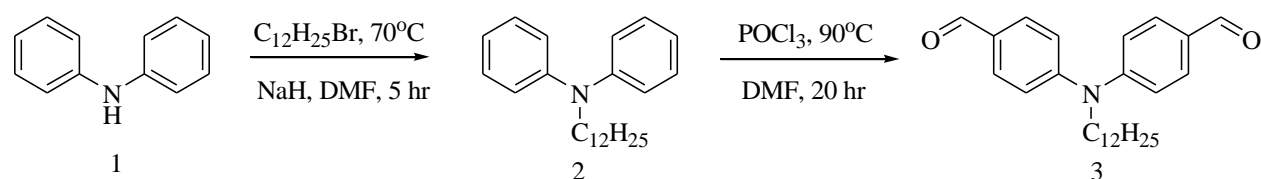
Synthesis of donor-acceptor conjugated molecule:
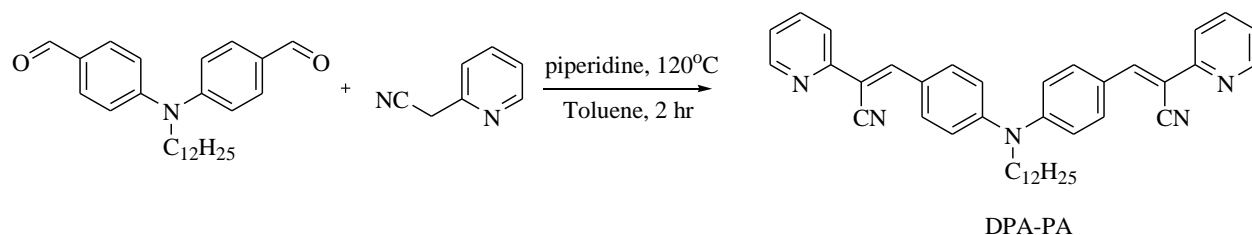
Scheme. 1 Synthesis route to the donor and conjugated DPA-PA molecule.

The final product was synthesized from compound 3 and 2-Acetonitryl pyridine in presence of piperidine. The FT-IR spectrum of DPA-PA was shown in Figure. 1. Newly formed cyano vinylene proton was observed at 8.6 ppm in ^{1}H NMR shown in Figure. 2. The FT-IR spectrum of the final product (DPA-PA) displayed a peak at 2215 cm^{-1}, which represents the presence of cyano groups. Bases on these results, we successfully synthesized and characterized of the target molecule.
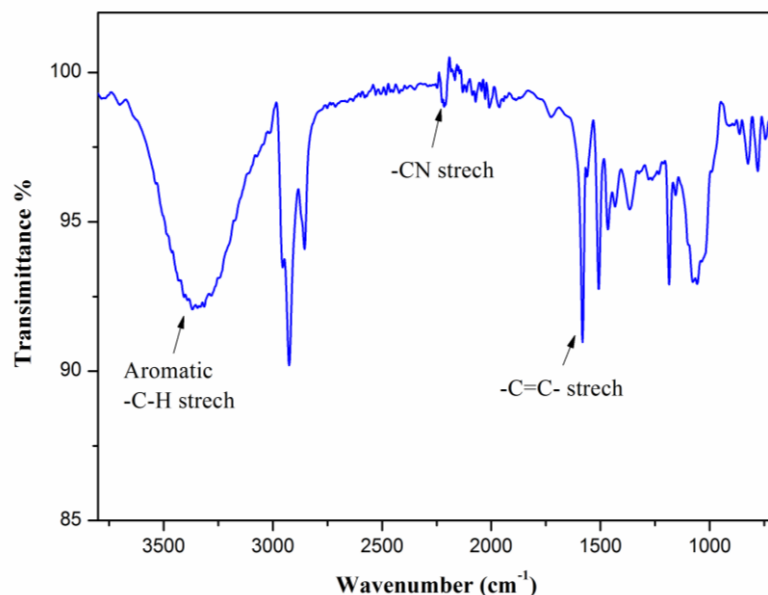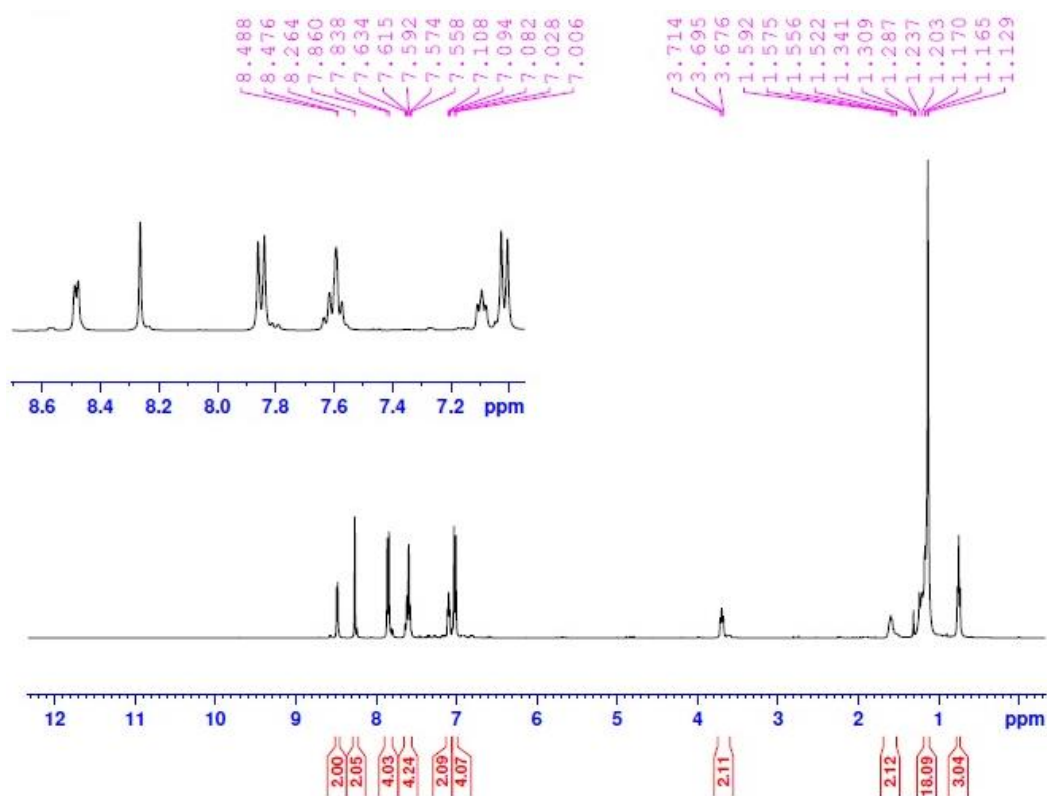

**Figure 1.** FT-IR spectra of the DPA-PA.

Figure 2. ^{1}H NMR spectra of the DPA-PA.

3.2 Optical characterization

3.2.1 Absorption studies. The optical and photophysical properties of DPA-PA were investigated by UV-visible absorption spectroscopy in dilute chloroform solution (10^{-5} M) and thin film, which was shown in Figure. 3. The DPA-PA has exhibited two types of absorption peaks. This is the common feature in donor-acceptor based conjugated molecules [15]. The first absorption peak was observed at lower wavelength side, which was appeared at 272 nm, and second absorption peak was observed at higher wavelength side, which was appeared at 433 nm. The higher energy peak of 272 nm was due to π-π^* electronic transition of the conjugation. The lower energy peak of 433 nm was attributed to intramolecular charge transfer (n-π^*) between the electron donating diphenylamine and electron withdrawing cyanopyridine. It was higher wavelength than previously reported diphenyl amine-carbazole based molecules [16]. Upon going to thin film absorption spectra appeared as broad peak when contrasted with solution absorption spectra. This establishes the thin film state having intermolecular interactions.
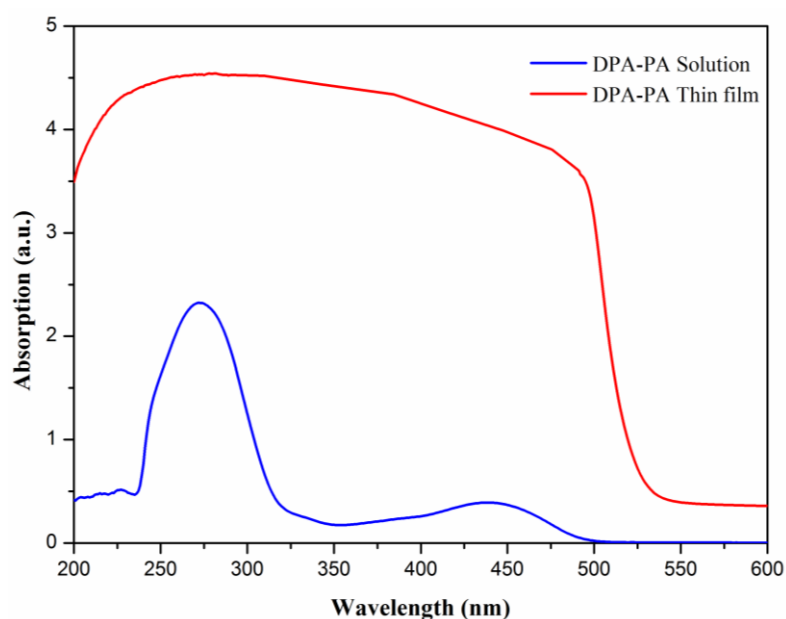
Figure 3. UV-visible spectra of DPA-PA in chloroform solvents and thin film.

The optical band gap value of the product was calculated from the absorption onset value of thin film according to the equation E_g^{opt} = 1240/ absorption onset value [17]. The optical band gap value was calculated as 2.2 eV. Moreover, we measured absorption value of the product in different solvents showed in table 1.

DPA-PA	Toluene (nm)	Diethyl ether (nm)	DCM (nm)	THF (nm)	Ethyl acetate (nm)	Acetone (nm)	Acetonitrile (nm)	DMF (nm)
π-π^*	290	276	275	260	275	272	275	262
n-π^*	433	427	433	433	433	433	433	441

Table. 1. UV-visible absorption maxima of DPA-PA in different solvents

3.2.2 Fluorescence studies. The fluorescence study of DPA-PA was observed in different solvents (nonpolar to polar) such as toluene, diethyl ether, dichloromethane, tetrahydrofuran, ethyl acetate, acetone, acetonitrile, and DMF. The product displayed high emission fluorescence behavior in various solvents when irradiated with long UV light (Figure. 4). The product displayed a strong solvatochromic effect [18]. It was exhibited green fluorescence color in nonpolar solvents. While increasing the polarity of solvents green fluorescence was shifted to yellow and orange fluorescence, it was clearly depicted in Figure. 4. The fluorescence spectra of DPA-PA in different solvents were shown in Figure. 5. The emission maximum was observed at 494 nm in a nonpolar solvent (toluene). While increasing solvent polarity the emission maxima also red shifted (532 nm for DMF), it was supported by fluorescence image (Figure. 4). This type of solvatochromism is called as a positive solvatochromism. Due to one kind of chromophore product exhibited a pure fluorescence emission spectra without any shoulder peak. The thin film absorption spectrum of DPA-PA was exhibited broad emission peak due to strong intramolecular interactions. The emission maxima of the thin film were observed at 541 nm.
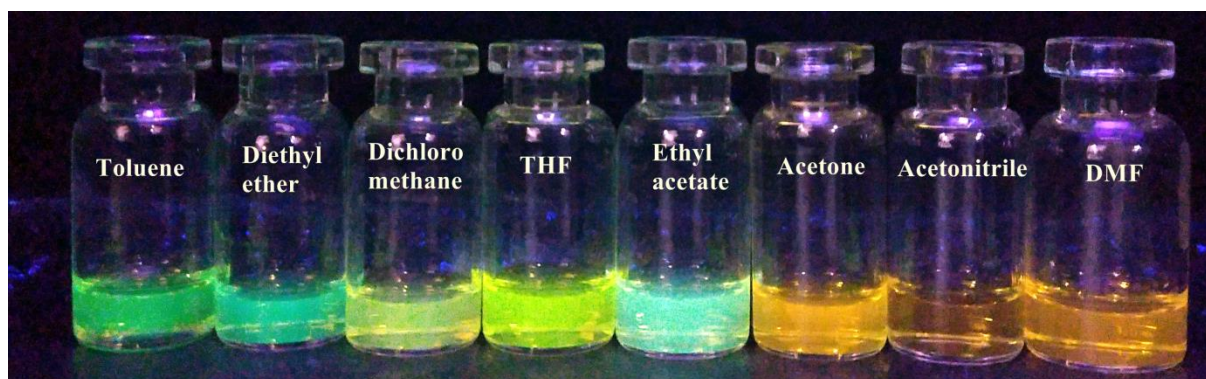

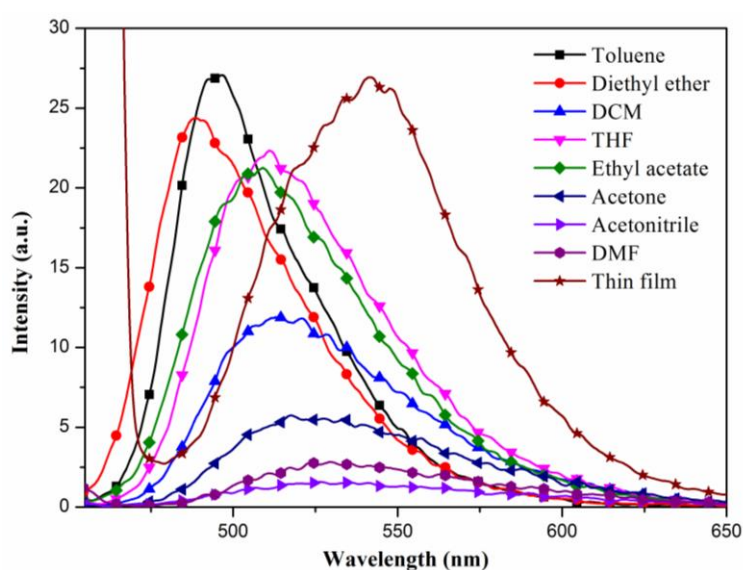**Figure 4**. Fluorescence of DPA-PA in different solvents

Figure 5. Fluorescence spectra of DPA-PA in different solvents and thin film.

Stokes shift is the difference between the point of the emission maxima and absorption maxima. If the Stokes shift is very less, the overlying of absorption and emission spectra will be more, it leads to decreases the luminescent efficiency [19]. In our study, stoke shift of DPA-PA was found to have 80 nm in THF solution. So this type of longer stokes shift compounds considered as the best compound for organic light emitting diodes.

3.3. Electrochemical studies

The electrochemical property of DPA-PA was explored by cyclic voltammetry measurements as shown in Figure. 6. The onset oxidation and onset reduction potentials have been measured with three electrode system. Ag/Ag$^+$ electrode used as a reference electrode, the platinum wire used as a counter electrode and DPA-PA coated ITO glass used as working electrode. The HOMO and LUMO energy levels were calculated from fallowing empirical equation [20].

E_{HOMO} (eV) = -q (E_{ox} + 4.7)

E_{LUMO} (eV) = -q (E_{red} + 4.7)

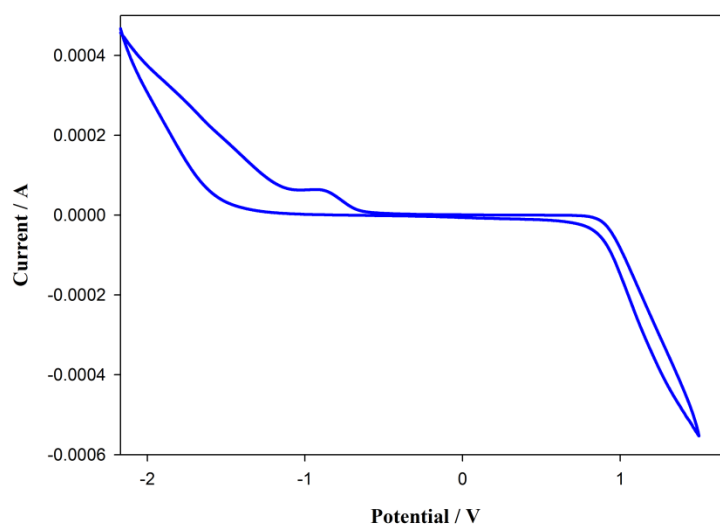E_g = E_{HOMO} − E_{LUMO}

Figure 6. Cyclic voltammogram of DPA-PA thin film on ITO glass in 0.1 M Bu$_4$NPF$_6$, CH$_3$CN solution with a scan rate 50 mV/s.

The onset oxidation and reduction potentials of DPA-PA are 0.85 V and -0.70 V respectively. The HOMO and LUMO energy levels of DPA-PA are calculated as -5.25 and -3.70 eV respectively. The lower LUMO for DPA-PA is attributed dodecyl side chain. The electrochemical band gap was calculated as 1.55 eV from HOMO and LUMO values. Successfully we achieved very lower band gap value for smaller molecule when compared to diphenylamine-malononitrile compounds [21]. The higher oxidation value (-4.9 eV) of DPA-PA due to electron-withdrawing molecule was attached to the conjugated system. The electron density in the π system of the conjugated backbone will be decreased due to pyridyl acetonitrile. Subsequently, the conjugated molecule (DPA-PA) will be stabilized and its oxidation value will be elevated. These types of low band gap conjugated molecules will be worked as a good capability in the area of photovoltaic applications [22].

4. Conclusion

We have successfully synthesized and characterized the diphenylamine-pyridyl acetonitrile based donor-acceptor based conjugated small molecule through Knoevenagel condensation. We have

achieved excellent solubility in all solvents due to successful incorporation of the dodecyl alkyl chain. The UV-visible absorption maxima of DPA-PA were observed at 433 nm. The Even small molecule can exhibit excellent green color fluorescence at 513 nm. The lower electrochemical band gap 1.55 eV achieved by the incorporation of pyridine acceptor. The results of synthesized conjugated small molecule will be promised for future photovoltaic applications.

Acknowledgement

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