SYNTHESIS AND SPECTRAL CHARACTERISATION OF D-A BASED CYANO-STILBENE DERIVATIVES, FOR ORGANIC SOLAR CELL APPLICATIONS

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SYNTHESIS AND SPECTRAL CHARACTERISATION OF D-A BASED CYANO-STILBENE DERIVATIVES, FOR ORGANIC SOLAR CELL APPLICATIONS

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ABSTRACT

1, 2-diphenylethene is called as stilbene. We synthesized ten donor acceptor based (D-A) cyano-stilbene derivatives and the structure was confirmed by ^{1}H-NMR, GC-MS, FT-IR. The absorption was calculated by UV-Visible spectrometer. From the UV-Vis study the stilbenes are having broad and strong absorption in the UV-Visible region. The strong and broad absorption in the UV-Visible region is the desired property for the high power conversion efficiency (PCE) organic photovoltaic (OPV).

Keywords: Acceptor, cyano-stilbene, donor, organic photovoltaic, and power conversion efficiency.

1. INTRODUCTION

In Greek colourful and shinning compounds are called as ‘stilbos’. The stilbene name was derived from the Greek word ‘stilbos’. Stilbene derivatives can be easily prepared by some conventional and eco-friendly methods. They are thermally and chemically stable, and possess absorption and fluorescence properties. The stilbene are mainly present in two isomeric forms namely trans-stilbene (E) and cis-stilbene (Z). In the above two forms trans form is more stable than compared with cis form because of steric factor and high energy in the later isomer. The two isomers are in equilibrium at room temperature but at high temperature or exposed to light the trans form is predominant because of the stability and energy difference. The energy of cis form higher than the trans form. The stilbenes are having same chemical properties but different physical properties like melting point, boiling point and refractive index and etc. They are insoluble in water but soluble in most of the common organic solvents [1].

Stilbenes are widely used in the manufacture of industrial dyes, dye lasers, optical brighteners, phosphor materials, scintillator and other materials. Donor– acceptor (D–π–A) dyestuff and colorants represent a vast majority of organic chromogens. Some of these compounds are also used as sources of dye laser radiation [2–3]. They are playing an increasingly prominent role in the area of photophysical, photochemical, biophysical and biomedical investigations. Un-substituted Stilbenes are less reactive but if any hydroxyl or some other functional group present in the stilbene it is highly reactive. Stilbenoids (hydroxylated derivatives of stilbene) are produced by plants are used as an important antibiotic material in their life time. The stilbene derivatives have also medical and biological activities, such as anti-microbial, antifungal, insecticidal and anti-inflammatory [4–5].

Stilbenes can be synthesized by many methods in that most important methods are given as follows, Aldol-type condensation, Wittig–Horner reaction, Perkin reaction, Negishi–Stille reactions and Heck reaction. In the above mentioned methods Aldol-type condensation between an aromatic aldehyde with active methylarene compound is most common because of economically benign, simple and easy way of preparation in short span of time [6-10]. The Aldol condensation type of stilbene synthesis involves the formation of carbanion and addition to the carbonyl group. The strong or weak base like Sodium hydroxide, pyridine or piperidine initiates the reaction by deprotonation of active methylarene. The carbanion then adds to carbon atoms of the carbonyl group of the aldehyde. The yield of the Aldol type stilbene synthesis is moderate. [11-14]

Broad and strong absorption band in visible and near infrared region to match the solar spectrum for increasing short circuit current (Jsc) [15]. A broad class of dyestuff and colorants are based on electron donor-acceptor (D-π-A) chromogens were synthesized by M. Asiri [16]. The stilbene dyes have a very wide absorption in UV-Visible range (200-600 nm). Due to the broad absorption in UV- Visible region stilbenes can be used as an efficient dye for organic photovoltaic. This observation leads us to synthesis stilbene dyes for the applications in organic photovoltaic.

2. MATERIALS AND METHODS

2.1 Materials

Thiophene-2-carboxaldehyde, Furfural, 4-hydroxybenzaldehyde, 4-bromobenzaldehyde, 5-bromothiophenecarboxaldehyde, Vanillin, 5-bromothiopheneacetonitrile, 4- hydroxyphenylacetonitrile, 4-fluorophenylacetonitrile, 4-nitrophenylacetonitrile, Potassium tert-butoxide and Ethanol were purchased from Sd-Fine chem. Ltd. All the solvents were distilled prior to usage.

General scheme for the synthesis of stilbene

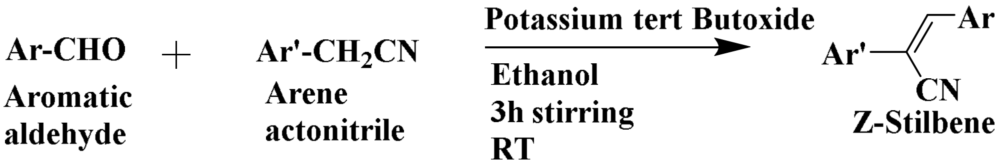
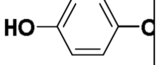
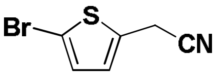
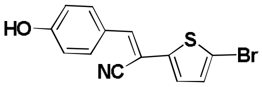
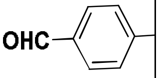
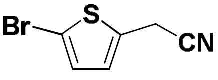
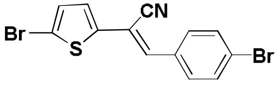
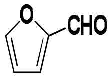
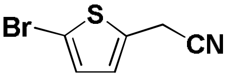
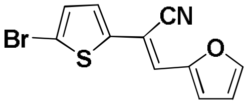
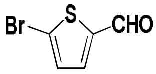
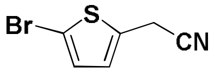
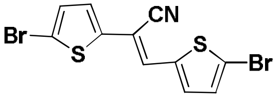
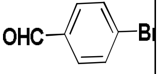
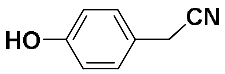
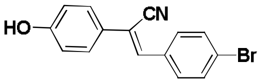
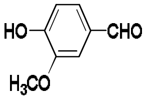
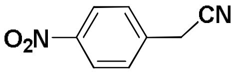
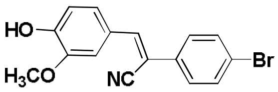
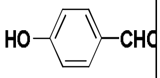
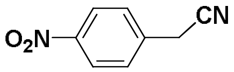
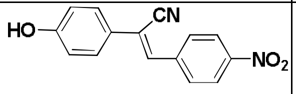
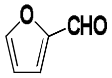
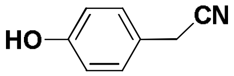
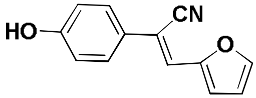
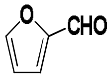
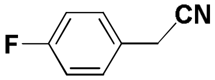
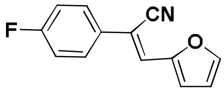
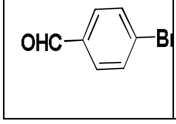
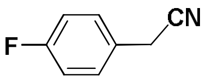
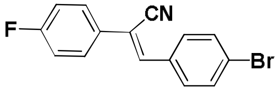


Table-1: Consolidated data for the stilbene synthesis:

Ar	Ar'	E- Stilbenes	Yield %	m.p ^{0}C	Colour	Stilbenes
			95	170	Brown	S-1
			87	220	Golden yellow	S-2
			83	90	Greenish yellow	S-3
			90	110	Light Yellow	S-4
			97	190	Light Yellow	S-5
			55	190	Reddish brown	S-6
			58	217	Dark yellow	S-7
			63	140	Yellow	S-8
			90	84	Brownish yellow	S-9
			88	86	Light yellow	S-10

2.2 Methodology

Cyanostilbene Synthesis

Aryl acetonitrile (20 mmol) was dissolved in 20 mL of ethanol and taken in a three neck flask. To this 10 mmol of alcoholic potassium tert-butoxide was added and stirred for half an hour. An alcoholic solution of aromatic aldehyde (20 mmol) was added drop wise into the above solution. Within a few minutes formation of coloured product was started. The reaction mixture was again stirred for 3 h at room temperature. Progress was monitored by TLC. The reaction mixture was then poured into crushed ice and neutralized with sufficient amount of water. The precipitated product was filtered by using a Buckner funnel. The filtered stilbene was washed with water and ethanol for several times to eliminate the sodium hydroxide and unreacted reactants present in the mixture respectively. The product was further purified by recrystallization in ethanol. Melting point of the stilbene checked. The product formation was further confirmed by the GC-MS, UV-Visible, FT-IR and ^{1}H-NMR spectra's. The consolidated data for the synthesized cyano-stilbenes were summarized in Table **1**.

1. Spectral characterization of (E)-2-(5-bromothiophen-2-yl)-3-(4-hydroxyphenyl)acrylonitrile

Brown color stilbene. FT-IR (KBr, cm^{-1}): 3303($\nu_{O\text{-}H}$), 2945(Ar $\nu_{C\text{-}H}$), 2270 ($\nu_{C\text{-}N}$), 1487, 1429 (Ar $\nu_{C=C}$), 615 ($\nu_{C\text{-}Br}$),cm^{-1}. ^{1}H-NMR [400 MHz, $CDCl_3$, δ=7.26 ppm, s]: 7.7 (2H, d), 7.3 (1H, d), 7.3 (IH, d), 7.2 (1H, s), 7.0 (1H, q), 6.9 (2H, d) was shown in Fig 1. M. F: $C_{13}H_9ONS$, calculated mass- 305, observed mass- 306. Yield: 95%, m.p-170 ^{0}C. The absorption spectra of S-1 was shown in Fig. 2.

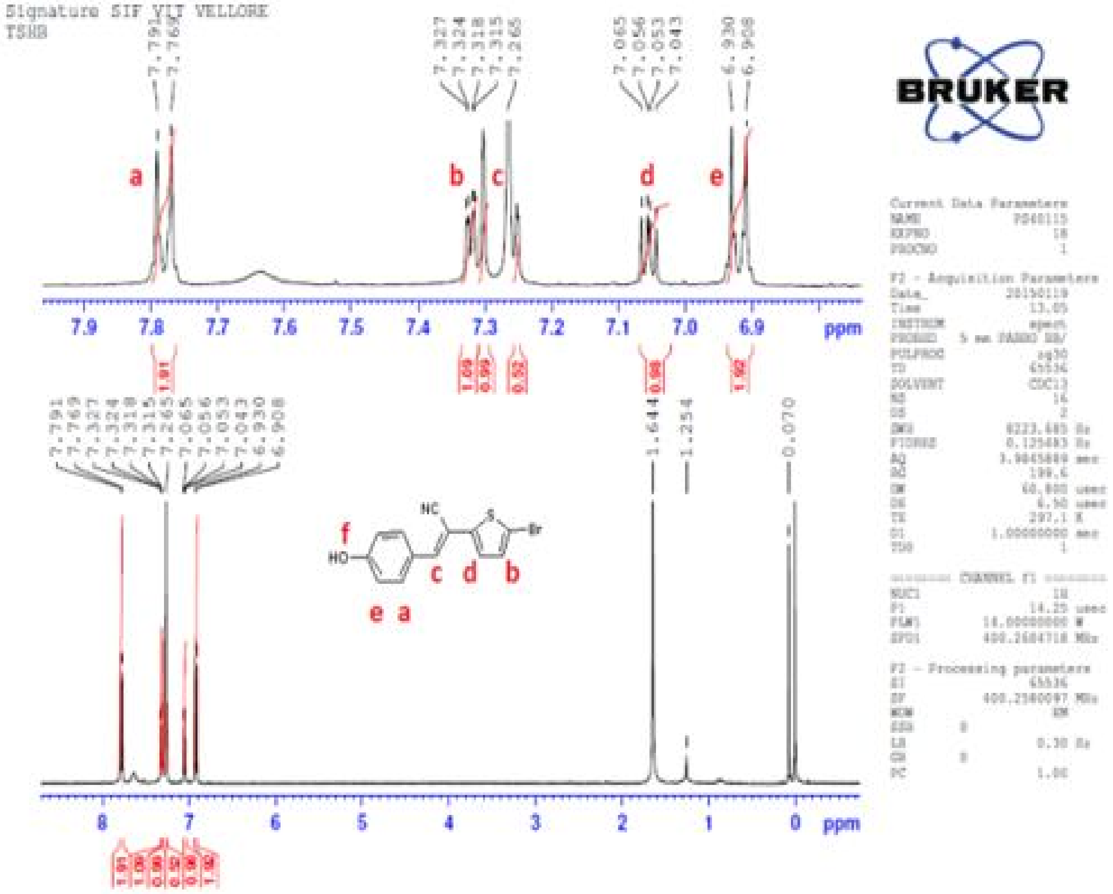


Fig-1: ^{1}H-NMR spectra of (E)-2-(5-bromothiophen-2-yl)-3-(4-hydroxyphenyl)acrylonitrile.

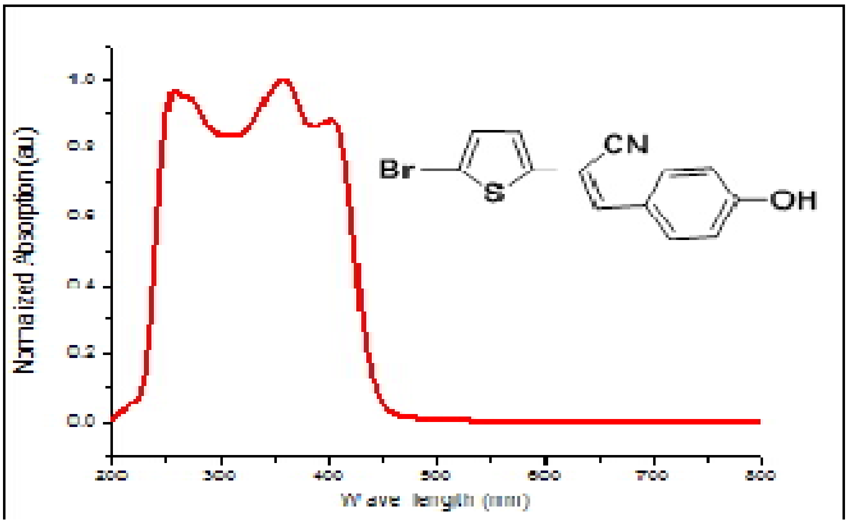


Fig-2: UV-Visible spectra of (E)-2-(5-bromothiophen-2-yl)-3-(4-hydroxyphenyl)acrylonitrile in chloroform.

2. Spectral characterization of (E)-3-(4-Bromophenyl)-2-(5-bromophen-2-yl)acrylonitrile

Golden yellow colour stilbene. FT-IR (KBr, cm^{-1}): 3034 (Ar $\nu_{C\text{-}H}$), 2223 ($\nu_{C\text{-}N}$), 1587, 1581, 1487 (Ar $\nu_{C=C}$), 810 ($\nu_{C\text{-}Br}$). ^{1}H-NMR [400 MHz, $CDCl_3$, δ=7.26 ppm, s]: 7.7 (2H, s), 7.5 (2H, d), 7.1 (2H, t), 7.0 (1H, d) was shown in Fig. 3. M. F: $C_{13}H_7Br_2NS$, calculated mass- 367, observed mass- 367.Yield: 87%, m.p- 220 ^{0}C. The absorption spectra of S-1 was shown in Fig. 4.

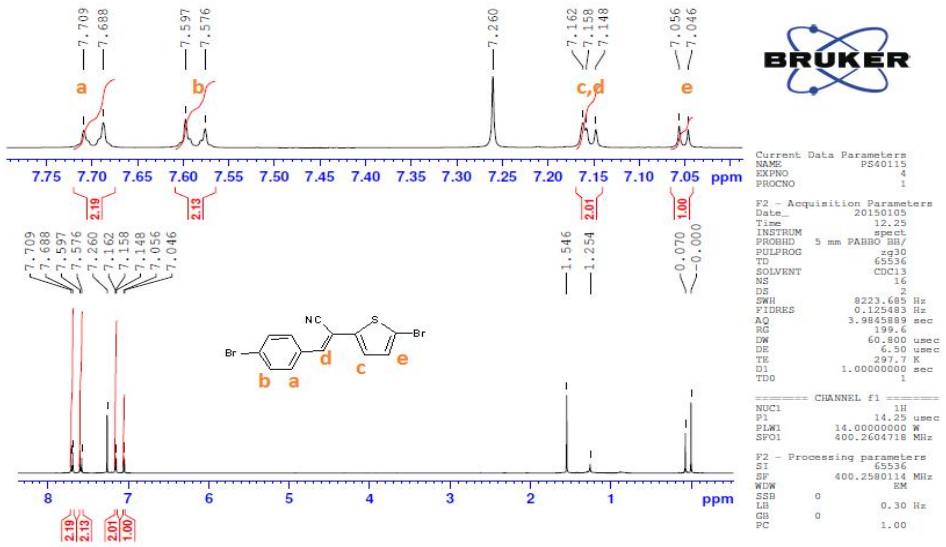


Fig-3:^{1}H-NMR spectra of (E)-3-(4-Bromophenyl)-2-(5-bromophen-2-yl)acrylonitrile.

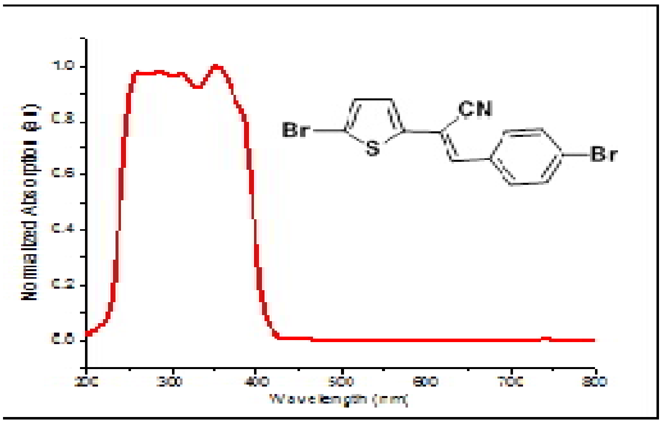


Fig-4: UV-Visible spectrum of (E)-3-(4-Bromophenyl)-2-(5-bromophen-2-yl)acrylonitrile in chloroform.

3. Spectral characterization of (E)-3-(4-Bromophenyl)-2-(5-bromophen-2-yl)acrylonitrile

Greenish yellow colour stilbene. FT-IR (KBr, cm^{-1}): 2945 (Ar ν_{C-H}), 2227 (Ar ν_{C-N}), 1487, 1429 (Ar $\nu_{C=C}$), 695 (ν_{C-Br}). ^{1}H-NMR [400 MHz, $CDCl_3$, δ=7.26 ppm, s]: 7.6 (1H, d), 7.1 (2H, d), 7.0 (2H, t), 6.5 (1H, q) was shown in Fig. 5. M. F: $C_{13}H_7Br_2NS$, calculated mass- 278, observed mass- 279. Yield: 83%, m.p- 90 ^{0}C.

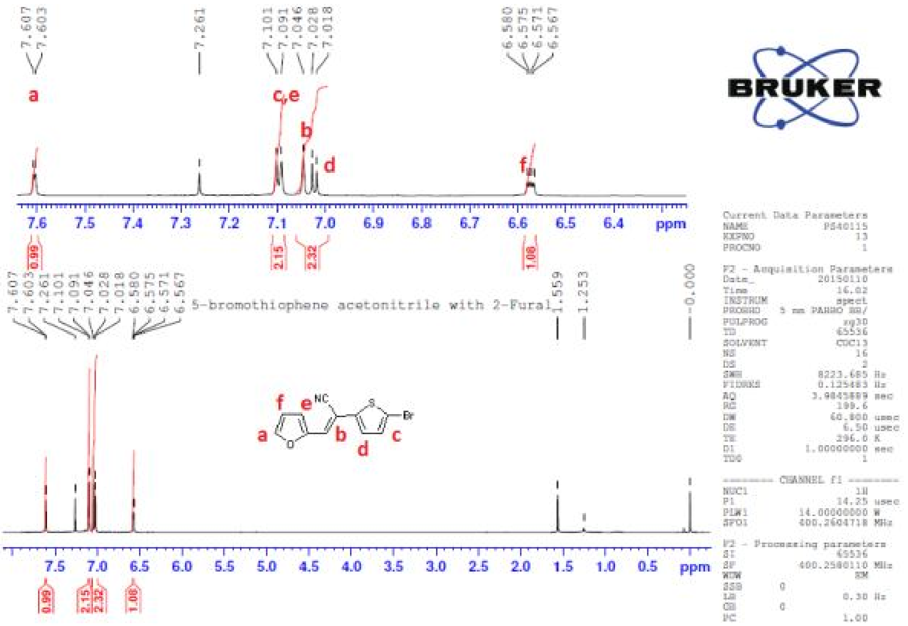


Fig-5: ^{1}H-NMR spectra of (E)-3-(4-Bromophenyl)-2-(5-bromophen-2-yl) acrylonitrile.

4. Spectral characterization of (E)-2,3-bis(5-bromothiophen-2-yl)acrylonitrile

Light yellow colour stilbene. FT-IR (KBr, cm^{-1}): 3305 (Ar $\nu_{C\text{-}H}$), 2231 ($\nu_{C\text{-}N}$), 1583, 1610, 1514 (Ar $\nu_{C=C}$), 821 ($\nu_{C\text{-}Br}$). ^{1}H-NMR [400 MHz, $CDCl_3$, δ=7.26 ppm, s]: 7.27 (2H, d), 7.1 (2H, t), 7.0 (1H, d) was shown in Fig. 6. M. F: $C_{11}H_5Br_2NS_2$, calculated mass- 372, observed mass- 373. Yield: 83%, m.p- 90 ^{0}C. The absorption spectra of S-1 was shown in Fig. 7.

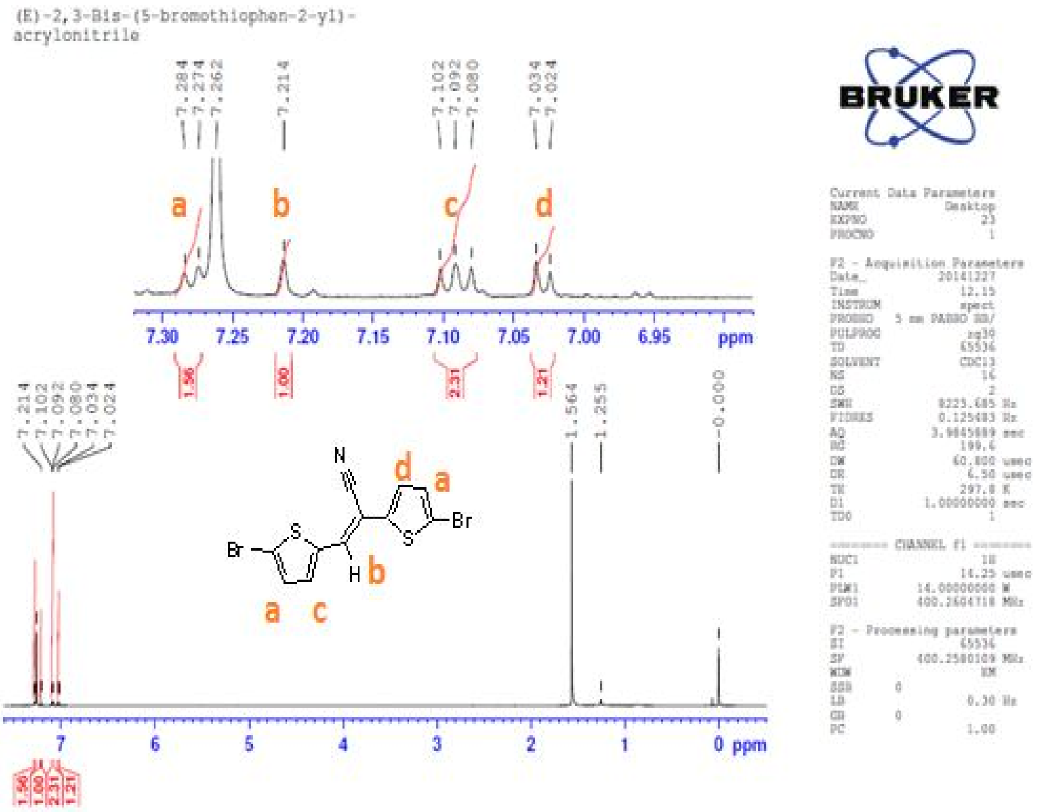


Fig-6: ^{1}H-NMR spectra of (E)-2,3-bis(5-bromothiophen-2-yl)acrylonitrile.

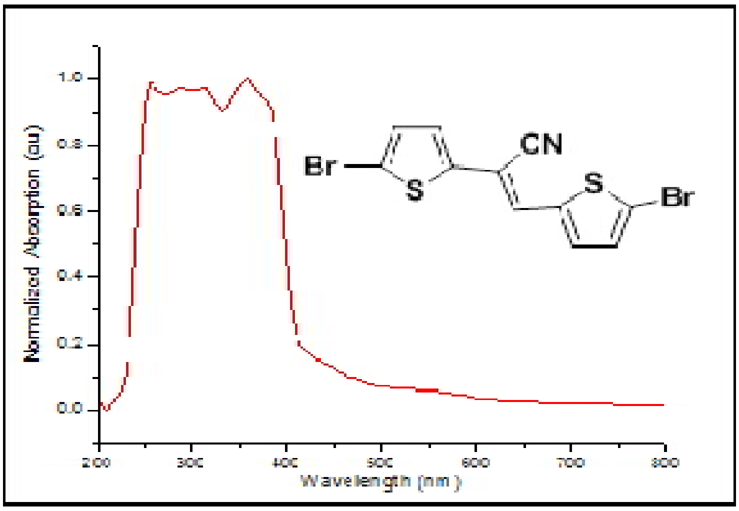


Fig-7: UV-Visible spectra of (E)-2,3-bis(5-bromothiophen-2-yl)acrylonitrile in chloroform.

5. Spectral characterization of (E)-3-(4-bromophenyl)-2-(4-hydroxyphenyl) acrylonitrile

Light yellow colour stilbene. FT-IR (KBr, cm^{-1}): 3379, 3338 ($\nu_{O\text{-}H}$), 3230 (Ar $\nu_{C\text{-}H}$), 2227 ($\nu_{C\text{-}N}$), 1610, 1583 ($\nu_{C=C}$), 821 ($\nu_{C\text{-}Br}$). ^{1}H-NMR [400 MHz, $CDCl_3$, δ=7.26 ppm, s]: 7.7 (2H, d), 7.5 (4H, t), 7.3 (1H, s), 6.9 (2H, d), 5.3 (1H, s) was shown in Fig. 8. M. F: $C_{15}H_{10}BrNO$, calculated mass- 298, observed mass- 299. Yield: 55%, m.p- 190 ^{0}C.

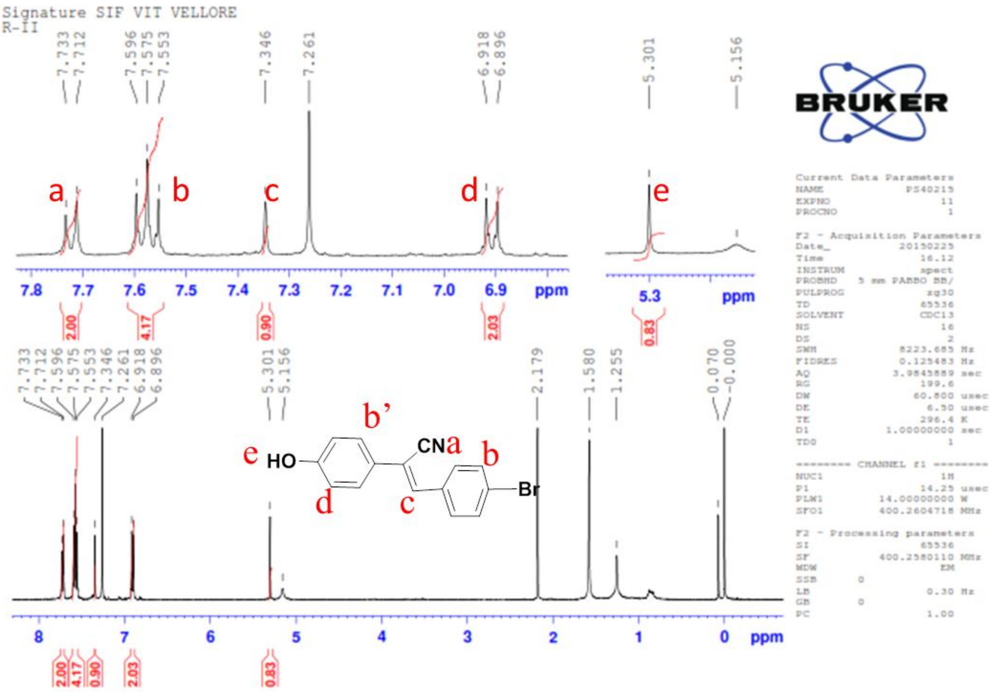


Fig-8: ^{1}H-NMR spectra of (E)-3-(4-bromophenyl)-2-(4-hydroxyphenyl) acrylonitrile.

6. Spectral characterization of (E)-3-(4-hydroxy-3-methoxyphenyl)-2-(4-nitrophenyl) acrylonitrile

Reddish brown colour stilbene. FT-IR (KBr, cm^{-1}): 3130 ($\nu_{O\text{-}H}$), 3094 (Ar $\nu_{C\text{-}H}$) 2227, ($\nu_{C\text{-}N}$), 1610 ($\nu_{C\text{-}O\text{-}C}$), 1570 ($\nu_{C=O}$), 1215 ($\nu_{N\text{-}O}$) ^{1}H-NMR [400 MHz, $CDCl_3$, δ=7.26 ppm, s]: 8.3 (2H, q), 7.84 (2H, q), 7.80 (1H, s), 7.6 (1H, s), 7.3 (1H, q) , 7.0 (1H, d), 6.0 (1H, s), 4.0 (2H, s) was shown in Fig. 9. M. F: $C_{16}H_{12}N_2O_4$, calculated mass- 296, observed mass- 297. Yield: 55%, m.p- 190 ^{0}C.

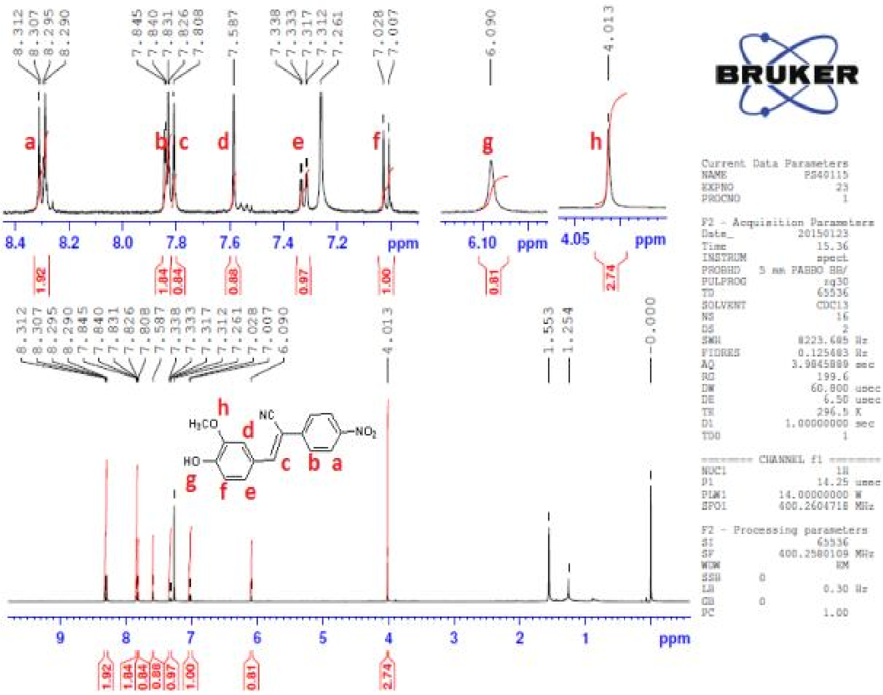


Fig-9: ^{1}H-NMR spectra of (E)-3-(4-hydroxy-3-methoxyphenyl)-2-(4-nitrophenyl) acrylonitrile.

7. Spectral characterization of (E)-2-(4-hydroxyphenyl)-3-(4-nitrophenyl)acrylonitrile

Yellow colour stilbene. FT-IR (KBr, cm^{-1}): 3404 ($\nu_{O\text{-}H}$), 2214 ($\nu_{C\text{-}N}$), 1585, (Ar $\nu_{C=C}$), 1512 ($\nu_{N=O}$). ^{1}H-NMR [400 MHz, $CDCl_3$, δ=7.26 ppm, s]: 8.3 (2H, d), 7.9 (2H, d), 7.8 (2H, d), 7.6 (1H, s), 6.9 (2H, d) was shown in Fig. 10. M. F: $C_{15}H_{10}N_2O_3$. Calculated mass-266, observed mass-267. Yield: 55%, m.p- 190 ^{0}C.

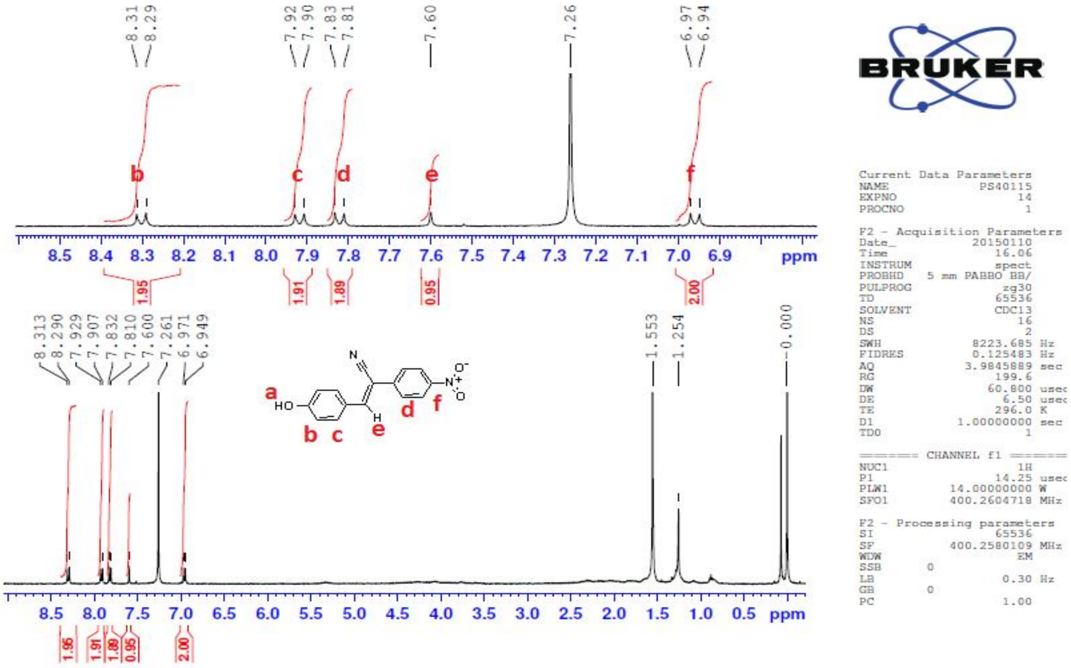


Fig-10: ^{1}H-NMR spectra of (E)-2-(4-hydroxyphenyl)-3-(4-nitrophenyl)acrylonitrile

8. Spectral characterization of (E)-3-(furan-2-yl)-2-(4-hydroxyphenyl) Acrylonitrile

Yellow colour stilbene. FT-IR (KBr, cm^{-1}): 3269 (Ar ν_{C-H}), 2227 (ν_{C-N}), 1614, 1591 ($\nu_{C=O}$), 1514 (ν_{C-Br}). ^{1}H-NMR [400 MHz, $CDCl_3$, δ=7.26 ppm, s]: 7.8 (1H, d), 7.6 (1H, s), 7.5 (2H, d), 7.0 (1H, d), 6.7 (3H, m), 5.3 (1H, s). M. F: $C_{16}H_{12}N_2O_4$, calculated mass-296, observed mass-297.Yield: 55%, m.p-190 ^{0}C.

9. Spectral characterization of (E)-2-(4-fluorophenyl)-3-(furan-2-yl) acrylonitrile

Light yellow colour stilbene. FT-IR (KBr, cm^{-1}): 3156 (Ar ν_{C-H}), 2337 (ν_{C-N}), 748, 588 (ν_{C-F}). ^{1}H-NMR [400 MHz, $CDCl_3$, δ=7.26 ppm, s]: 7.8 (2H, d), 7.6 (H, s), 7.3 (2H, d), 7.1 (2H, d), 6.9 (1H, d) , 6.4 (1H, s). M. F: $C_{13}H_8FNO$, Calculated mass- 213, observed mass- 214.Yield: 55%, m.p- 190 ^{0}C.

10. Spectral characterization of (E)-2-(4-fluorophenyl)-3-(furan-2-yl) acrylonitrile

Light yellow colour stilbene. FT-IR (KBr, cm^{-1}): 3026 (Ar ν_{C-H}), 2216 (ν_{C-N}), 1834, ($\nu_{C=C}$), 1512, (ν_{C-N})1246, (ν_{C-Br})1078 (ν_{C-F}). ^{1}H-NMR [400 MHz, $CDCl_3$, δ=7.26 ppm, s]: 7.9 (2H, d), 7.8 (1H, s), 7.6 (2H, d), 7.5 (2H, d), 7.01 (2H, d) , 6.4 (1H, s). M. F: $C_{15}H_9BrFN$, calculated mass- 300, observed mass- 302. Yield: 55%, m.p- 190 ^{0}C.

3. RESULTS AND DISCUSSION

Cyano-stilbene are most widely used in organtic solar cell to construct a D-A acceptor system with broad absorption in the UV-vis region. In the paper we reported synthesis and studies of some of cyano-stilbene derivatives. From the FT-IR, we confirmed the functional groups such as –OH, -CN, $-NO_2$, and -C=C-. NMR spectroscopic techniques we used to confirm the product formation. The Gas chromatography with mass spectroscopy was used to find the product formation with yield.

4. CONCLUSION

We synthesized a donor- acceptor based cyano-stilbene derivatives from an aromatic aldehyde and aryl acetonitrile by an efficient Aldol condensation method using alcoholic alkali as a catalyst. We got moderate-good yields. The formation of the stilbene was confirmed by the ^{1}H-NMR, GC-MS, FT-I.R and melting point. Calculated mass clearly matched with the observed GC-Mass. ^{1}H-NMR also confirms the formation of product and its purity. UV-Visible absorption studies revealed that broad and stronger absorption of cyano-stilbenes. The strong and broad absorption is the desired property for the high PCE organic photovoltaic. From the electronic absorption studies it is clear our molecule could be a good harvester of solar radiations. In future we are planned to use this dyes as a good light harvester in organic solar cells.

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