Chapter 2  
Part-B: Synthesis and Studies of Dicyanovinylenecarbazole-Based A-D-A Conjugated Small Molecules for Organic Solar Cell Applications

2.5 INTRODUCTION

The small molecules or polymers used as a donor for organic solar cell and both the donor molecules are having unique advantages in the past few years, immense improvement is going on polymer solar cell, and its achieved maximum power conversion efficiencies (PCEs) at ~10.8% (Liu et al., 2014). Recent day’s great progress in small molecule also, Yongsheng et al., (2013) was reported highest PCE of 10.1% used as small donor molecules, which results are the BHJ device, very close to polymers. So far, it is still a significant competition between small molecule and polymers to get the highest efficiency used for organic solar cell applications. The small molecule having unique advantages is well-defined molecular structure, definite molecular weight, high purity, and improved batch-to-batch reproducibility (Chang et al., 2009). The challenges of the donor for organic solar cell its need for broadening absorption range towards NIR, reduce band gap, increase hole mobility, morphology control.

To improve the PCE of BHJ OSCs, the following parameters are kept in mind when designing a molecules structure. (1) Designed molecules need broader absorption range (the increment of absorption need more π conjugations). (2) Increase solubility by incorporate of an alkyl chain or thiophene spacers. (3) Low-lying HOMO energy levels, easily tuned electronic structures, and sufficient electron transport property (Bessette et al., 2014; Zhou et al., 2012). The designed novel donor materials are necessary to improve the maximum area coverage on the solar spectrum, its can help to enhance the PCEs. To improve high-performance OSCs, a popular and universal strategy is to design donor–(π-spacer)–acceptor (D–π–A) segment small molecules which can adjust the energy levels and increase the absorption properties due to their effective photoinduced intramolecular charge-transfer characteristics between donor and acceptor moiety. Nowadays many research groups are focusing on carbazole-based π-conjugated molecules, because of cheap starting materials, more thermal stability, higher hole mobility, high electron rich nature, excellent photoconductivity (Chu et al., 2009; Kim et al., 2011). Anandan et al., (2013) reported carbazole containing (D-π-A) type metal-free organic dye molecule are used for dye-sensitized solar cell (DSSCs) applications and the molecules are carbazole (donor unit) attached
different type of cyanovinylene containing acceptor units and it was fabricated DSSCs device showing high PCE of 2.37%, short circuit current of 5.18 mA cm$^{-2}$ and fill factor of 50.8%. Sharma et al., (2012) reported a series of carbazole-based polymers with 4-nitrophenylcyanovinylene unit and this polymer showed the HOMO energy level of -5.18 eV, enhance Voc of 11.25 V and PCE of 5.93%. Sharma et al., (2009) synthesized molecules designed mainly for a cyanovinylene 4-nitrophenyl acceptor unit attached to different donor units of dithienylcarbazole, pyran, triphenylamine, 1,3,5-triazine, dihexyloxyphenylene. The cyanovinylene, 4-nitrophenyl containing molecules are showed broad absorbance in the range of 350-700 nm and low band gap (LBG). In same group dihexyloxyphenylene attached cyanovinylene 4-nitrophenyl polymers showed optical band 1.65 eV and PCE of 5.07% (Mikroyannidis et al., 2009). Xue et al., (2014) reported tricycle based polymer-fullerene and carbazole combine with phenylcyanovinylene acceptor unit. Tai et al., (2012) reported cyanovinylene containing conjugated polymer of fluorene coupled with 3-(5-bromo thiophen-2-yl)-2-(thiophen-2-yl)acrylonitrile and cyanovinylene based polymers showed a deep-lying HOMO energy level of -5.61 eV. The fluorine and nitro atoms directly attached to the backbone of the small molecule have exhibited great improved efficiency of OSCs. Previously reported fluorine and nitro units containing donor molecules showed high open-circuit voltage ($V_{oc}$), and high PCE because of fluorine unit slightly larger than hydrogen and more electron withdrawing properties. The substitution of fluorine onto the molecules backbone reduced the HOMO energy levels of molecules when compared with the nonfluorinated analogues (Son et al., 2011). The electron-withdrawing unit of fluorine-containing conjugated polymers have attracted much attention, recently Ning et al., (2013) reported serious of fluorinated benzothiadiazole-based conjugated copolymers, they achieved maximum efficiency of 7.27% for BHJ Solar Cells device.

Although this (A-D-A) type small molecules have limited solubility in a common organic solvent at room temperature. It is well-known that incorporate of different side chains in small molecules play a vital role in certain key properties, such as solubility, inter- and intramolecular interactions, the charge transporting property, and morphology. The proper selection of side chains and π spacer enhance the excellent solubility. It’s very useful to uniform coating with acceptors PC$_{61}$BM / PC$_{71}$BM to make intermolecular interactions to form required morphology and this gain to obtain better film character and desired phase morphologies.
Therefore, we are focusing on fluorine and nitro containing conjugated small molecules synthesized and studied for OSCs. In this chapter, we report the carbazole containing (A-D-A) type small molecules; carbazole is an electron donor, which is attached with fluorine, nitro electron withdrawing group containing benzene as the acceptor to join with cyanovinylene spacers. In first step carbazole alkylated using hexyl, 2-ethyl hexyl chains. In this step distinctive side chains attached to carbazole units. A different alkyl chain has been introduced to improve solubility and stability of the molecules. The second step was formylated using DMF and POCl₃. In further step 4-fluorophenyl acetonitrile, 4-nitrophenyl acetonitrile was attached with 3,6-carbazole position simple knovenagal condensation reactions, it extend the π-conjugation of the carbazole, cyanovinylene attached in the 3rd and 6th positions to get (2Z,2’Z)-3,3’-(9-hexyl-9H-carbazole-3,6-diy)bis(2-(4-fluorophenyl)acrylonitrile) [FHCS], (2Z,2’Z)-3,3’-(9-hexyl-9H-carbazole-3,6-diy)bis(2-(4-nitrophenyl)acrylonitrile) [NHCS], (2Z,2’Z)-3,3’-(9-(2-ethylhexyl)-9H-carbazole-3,6-diy)bis(2-(4-fluorophenyl)acrylonitrile) [FBCS] and (2Z,2’Z)-3,3’-(9-(2-ethylhexyl)-9H-carbazole-3,6-diy)bis(2-(4-nitrophenyl)acrylonitrile) [NBCS]. The NHCS small molecules based on BHJ OSCs device showed maximum PCE of 0.90%.

2.6 EXPERIMENTAL

2.6.1 MATERIALS AND METHODS

Carbazole, 1-bromohexane, 2-ethyl hexyl bromide, were purchased from Sigma-Aldrich and Himedia Company. Phosphoryl chloride (POCl₃), dry dimethylformamide (DMF), dichloromethane, chloroform were obtained from SD Fine-Chem Limited. Potassium tert-butoxide, sodium hydroxide (NaOH), potassium hydroxide (KOH) was purchased from AVRA company. Other solvents were purchased commercially as AR-grade quality and used without further purification. Column chromatography was performed using silica gel Merck (60-120 mesh). The characterization methods have been followed by 2.2.2 measurements page no. 21.

2.6.2 SYNTHESIS OF SMALL MOLECULES FHCS, NHCS, FBCS, AND NBCS

The FHCS, NHCS, FBCS and NBCS were prepared as shown in Scheme 2.2. Compound Ia, Ib, Ia, and IIb prepared via the synthetic procedure reported previously (Sharma et al., 2012; Ramkumar et al., 2012). Compound IIa and IIb treating with 4-fluorophenylacetonitrile, 4-nitrophenylacetonitrile detailed procedures are as follows
2.6.2.1 SYNTHESIS OF 9-HEXYL-9H-CARBAZOLE (Ia)

Carbazole (3.30 g, 20 mmol), potassium hydroxide (2.96 g, 52.8 mmol) dissolved in DMF (40 mL) and then 1-bromohexane (3.30 g, 20 mmol) was added by dropwise. The reaction mixture was stirred at room temperature for 48 h. The reaction mixture was poured into water and extracted with chloroform and dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporator, the residue was recrystallized in n-hexane to afford compound Ia (4.8 g, 92%) as a white solid. $^1$H-NMR (400 MHz, CDCl$_3$, ppm): 8.11 (d, 2H), 7.46-7.42 (m, 2H), 7.42-7.39 (d, 2H), 7.26-7.20 (m, 2H), 4.31-4.28 (t, 2H), 1.88-1.85 (m, 2H), 1.41-1.37 (m, 6H), 0.86 (t, 3H).

2.6.2.2 SYNTHESIS OF 9-(2-ETHYLHEXYL)-9H-CARBAZOLE (Ib)

To the mixture of carbazole (5 g, 30 mmol) and sodium hydroxide (7.2 g, 185 mmol) were dissolved in 100 mL of DMSO and the reaction mixture was stirred at room temperature for 1 h. The 2-ethylhexyl bromide (6.9 g, 36 mmol) was added in a drop wise to the reaction mixture at room temperature for a period of 30 min. The resulting reaction mixture was further refluxed for 24 h. After cool to room temperature, the mixture was poured into water and the organic layer was
extracted with dichloromethane and dried over anhydrous magnesium sulfate. The crude product was further purified by column chromatography using hexane: ethyl acetate (9:1) as the eluent. Compound Ib (6.9 g, yield: 82%, Colorless oil). $^1$H-NMR (400 MHz, CDCl$_3$, ppm): 8.23 (d, 2H), 7.57 (t, 2H), 7.51 (d, 2H), 7.36-7.33 (t, 2H), 4.25-4.22 (m, 2H), 2.33-2.15 (m, 1H), 1.41-1.37 (m, 8H), 1.04 (m, 6H).

2.6.2.3 SYNTHESIS OF 9-HEXYL-9H-CARBAZOLE-3,6-DICARBALDEHYDE (IIa)

POCl$_3$ (25 mL, 0.27 mole) was added drop wise to DMF (35 mL, 0.45 mole) for 1 h at 0 °C. Compound Ia (4.00 g, 16 mmol) in dichloromethane (20 mL) was added to the above solution at room temperature after that increase the temperature to 90 °C stirred for 4 h. The reaction mixture was poured into ice-cubes and neutralized with NaOH solution. The solution was extracted three times with ethyl acetate and dried over anhydrous magnesium sulfate. The excess of dichloromethane was removed by vacuum distillation. The crude product was purified by column chromatography (eluent: hexane /ethyl acetate- 8:2) using silica gel afford compound IIa (2.9 g, Yield: 59%). $^1$H-NMR (CDCl$_3$, ppm): 10.13 (s, 2H), 8.67 (s, 2H), 8.09-8.07 (d, 2H), 7.56-7.54 (d, 2H), 4.40-4.36 (t, 2H), 1.93-1.89 (m, 2H), 1.38-1.34 (m, 6H), 0.86 (m, 3H).

2.6.2.4 SYNTHESIS OF 9-(2-ETHYLHEXYL)-9H-CARBAZOLE-3,6-DICARBALDEHYDE

POCl$_3$ (65 mL, 1.6 mole) was added drop wise to DMF (99 mL, 1.4 mole) and stirred at 0 °C about 1 h. Compound Ib (17.87 g, 0.64 moles) in dichloromethane (120 mL) was added to the above solution at room temperature after that increase the temperature to 90 °C stirred for 6 h and cool to room temperature. The reaction mixture was poured into ice-cubes and neutralized with an aqueous solution of NaOH. The solution was extracted three times with ethyl acetate and dried over anhydrous magnesium sulfate. The excess of dichloroethane was removed by vacuum distillation. The crude product was purified by column chromatography Hexane: Ethyl acetate (8:2) as the eluent. Compound IIb (8.8 g, yield: 41%, Yellowish solid). $^1$H-NMR (400 MHz, CDCl$_3$, ppm): 10.13 (s, 2H), 8.66 (s, 2H), 8.09-8.06 (d, 2H), 7.54-7.51 (d, 2H), 4.40-4.37 (t, 2H), 1.95-1.91 (m, 1H), 1.32 (m, 8H), 0.86 (m, 6H).

2.6.2.5 SYNTHESIS OF SMALL MOLECULES FHCS, AND FBBCS

The compound IIa (or) IIb (1 eq) and 4-fluorophenyl acetonitrile (2.2 eq) were taken in 100 mL three neck round bottom flask in absolute ethanol. A catalytic amount of potassium that-
butoxide was added to this mixture at room temperature under N₂ atm. The reaction mixture was stirred for 6 h at room temperature. It was monitored by TLC, excess ethanol was concentrated. A bright yellow solid was filtered and washed with cooled ethanol for 3 to 4 times. It was recrystallized in dichloromethane and methanol (1:1) to give the products.

2.6.2.6 SYNTHESIS OF FHCS

9-hexyl-9H-carbazole-3,6-dicarbaldehyde (0.16 g, 0.5 mmol), 4-fluorophenyl acetonitrile (0.13 g, 1.2 mmol) and potassium tert-butoxide was added, remaining procedure as same as above. Yellow solid (0.24 g, yield: 90%, 280-282 °C).¹H-NMR (400 MHz, CDCl₃, ppm): 8.64 (s, 2H), 8.19 (d, 2H), 7.71-7.68 (t, 4H), 7.68 (s, 2H), 7.51-7.49 (d, 2H), 7.18-7.14 (t, 4H), 4.36-4.34 (t, 2H), 1.93-1.90 (m, 2H), 1.41-1.37 (m, 6H), 0.86 (t, 3H).¹³C-NMR (400 MHz, CDCl₃): 143.12, 142.34, 131.44, 127.85, 127.77, 127.71, 125.83, 123.35, 123.00, 119.05, 116.41, 116.19, 110.18, 109.89, 107.47, 43.85, 31.14, 29.20, 27.11, 22.72, 14.20. FT-IR (cm⁻¹): 2929 (CH₃ stretch), 2208 (C triple bond N stretch), 1590 (C-C stretch aromatic), 1277, 826 (Alkyl halide).

2.6.2.7 SYNTHESIS OF FBCS

9-(2-ethylhexyl)-9H-carbazole-3,6-dicarbaldehyde (0.335 g, 1.0 mmol), 4-nitrophenyl acetonitrile (0.29 g, 2.2 mmol) and potassium tert-butoxide was added, remaining procedure as same as above. Yellow solid (0.84 g, yield: 84%, 160- 164 °C)¹H-NMR (400 MHz, CDCl₃, ppm): 8.63 (s, 2H), 8.19-8.17 (dd, 2H), 7.71-7.68 (t, 4H), 7.66 (s, 2H), 7.49-7.47 (d, 2H), 7.18-7.14 (t, 4H), 4.23-4.20 (t, 2H), 1.92-1.89 (m, 1H), 1.37-1.34 (m, 8H), 0.85 (t, 6H).¹³C-NMR (400 MHz, CDCl₃): 143.10, 142.79, 131.48, 131.45, 127.86, 127.78, 127.65, 125.83, 123.32, 122.98, 119.06, 116.42, 116.20, 110.18, 107.46, 48.09, 39.74, 31.23, 29.02, 24.64, 23.22, 14.22, 11.10. FT-IR (cm⁻¹): 2930 (CH₃ stretch), 2206 (C triple bond N stretch), 1587 (C-C stretch aromatic), 1238, 830 (Alkyl halide).

2.6.2.8 SYNTHESIS OF SMALL MOLECULES NHCS, AND NBCS

The compound IIa (or) IIb (1 eq) and 4-nitrophenylacetonitrile (2.2 eq) were taken in 100 mL three neck round bottom flask in absolute ethanol. The reactant was completely dissolved under heating condition after the catalytic amount of potassium tert-butoxide was added into the mixture at room temperature under N₂ atm. The reaction mixture was stirred at 60 °C for 6 h and cooled to room temperature. It was monitored by TLC, excess ethanol was concentrated. A bright
yellow solid was filtered and washed with cooled ethanol. It was recrystallized in dichloromethane and methanol (1:1) to give the products NHCS, and NBCS.

2.6.2.9 SYNTHESIS OF NHCS

9-hexyl-9H-carbazole-3,6-dicarbaldehyde IIa (0.52 g, 1.7 mmol), 4-nitrophenyl acetonitrile (0.60 g, 3.7 mmol) and potassium tert-butoxide was added remaining procedure as same as above. Orange color solid (0.60 g, yield: 60%). $^1$H-NMR (400 MHz, CDCl$_3$, ppm): 8.70 (s, 2H), 8.34-8.32 (d, 2H), 7.71-7.68 (t, 4H), 7.66 (s, 2H), 7.49-7.47 (d, 2H), 7.18-7.14 (t, 4H), 4.24-4.22 (t, 2H), 1.90-1.88 (m, 2H), 1.40-1.37 (m, 6H), 0.88 (t, 3H). FT-IR (cm$^{-1}$): 2931 (CH$_3$ stretch), 2208 (C triple bond N stretch), 1562 (C-C stretch aromatic), 1336, 852 (Alkyl).

2.6.2.10 SYNTHESIS OF NBCS

9-(2-ethylhexyl)-9H-carbazole-3,6-dicarbaldehyde (0.33 g, 1.0 mmol), 4-nitrophenyl acetonitrile (0.35 g, 2.2 mmol) and potassium tert-butoxide was added remaining procedure as same as above. Orange color solid (0.4 g, yield: 68%, 260-263 °C). $^1$H-NMR (400 MHz, CDCl$_3$, ppm): 8.70 (s, 2H), 8.34-8.32 (d, 2H), 7.71-7.68 (t, 4H), 7.66 (s, 2H), 7.49-7.47 (d, 2H), 7.18-7.14 (t, 4H), 4.23-4.20 (t, 2H), 1.92-1.89 (m, 1H), 1.37-1.34 (m, 8H), 0.85 (t, 6H). $^{13}$C-NMR (400 MHz, CDCl$_3$): 147.78, 146.16, 143.52, 141.45, 128.60, 126.58, 125.49, 124.63, 123.76, 123.48, 118.36, 110.59, 106.38, 48.27, 39.80, 31.24, 29.92, 24.66, 23.21, 14.20, 11.11. FT-IR (cm$^{-1}$): 2924 (CH$_3$ stretch), 2209 (C triple bond N stretch), 1573 (C-C stretch aromatic), 1338, 852 (Alkyl).

2.7 RESULTS AND DISCUSSIONS

2.7.1 SYNTHESIS AND CHARACTERIZATION OF THE SMALL MOLECULES

The small molecules (FHCS, NHCS, FBCS, and NBCS) synthetic procedures are outlined in Scheme 2.2. The alkylation of carbazole (Ia, Ib) was reported in literature (Ramkumar et al., 2013; Sharma et al., 2012). The important of introducing alkyl chain is to decrease the steric hindrance and increase the solubility and stability of the molecules. The obtained N-alkylation product was further formylated in the presence of DMF and POCl$_3$ by Vilsmeier–Haack formylation reaction. The cyanovinylene π-spacer was introduced in the 3rd and 6th positions of the carbazole ring by knovenagal condensation reactions gave good yields. It extends the π-conjugation to get small molecules FHCS, NHCS, FBCS, and NBCS. The four small molecules
are freely soluble in all common organic solvents such as dichloromethane, chloroform, chlorobenzene, tetrahydrofuran, and dichloromethane. The obtained small molecules structure was confirmed by NMR and FT-IR spectroscopic method and it showed in Fig 2.18-2.33.

Fig 2.18 $^1$H-NMR Spectrum of Compound IIb

Fig 2.19 FT-IR Spectrum of Compound FHCS
Fig 2.20 $^1$H-NMR Spectrum of Compound FHCS

Fig 2.21 $^{13}$C-NMR Spectrum of Compound FHCS
Fig 2.22 HRMS Spectrum of FHCS

Calculated mass = 541.23
Observed mass = 541.20

Fig 2.23 FT-IR Spectrum of Compound NHCS
Fig 2.24 $^1$H-NMR Spectrum of Compound NHCS

Fig 2.25 HRMS Spectrum of NHCS
Fig 2.26 FT-IR Spectrum of Compound FBCS

Fig 2.27 $^1$H-NMR Spectrum of Compound FBCS
Fig 2.28 $^{13}$C-NMR Spectrum of Compound FBCS

Calculated mass = 569.26
Observed mass = 569.23

Fig 2.29 HRMS Spectrum of FBCS
**Fig 2.30** FT-IR Spectrum of Compound NBCS

**Fig 2.31** $^1$H-NMR Spectrum of Compound NBCS
Fig 2.32 $^{13}$C-NMR Spectrum of Compound NBCS

Calculated mass = 623.25
Observed mass = 623.22

Fig 2.33 HRMS Spectrum of NBCS
2.7.2 THERMAL PROPERTIES OF THE SMALL MOLECULES

The thermal properties of the small molecule were investigated by thermogravimetric analysis (TGA) under a nitrogen atmosphere at a heating rate of 10 °C min$^{-1}$, as shown in Fig 2.34 and the results are summarized in Table 2.3 from the TGA curve 5% decomposition temperatures ($T_d$) of NHCS, FHCS, FBCS, and NBCS were 343, 373, 359 °C and 262 °C respectively. All the molecules showed good thermal stability and it’s sufficient for solar cell applications. Fig 2.35, showed the DSC curve of small molecules for FHCS, NHCS, FBCS and NBCS. The endothermic peaks were observed at 545, 563, 625 °C and 530 °C respectively.

2.7.3 PHOTOPHYSICAL PROPERTIES OF THE SMALL MOLECULES

The normalized UV-vis absorption spectra of the synthesized small molecules in dilute chloroform solution are showed in Fig 2.36, and summarized data are listed in Table 2.3. All the small molecules showed two absorption bands and the first absorbance bands range from 300-365 nm it indicates that $\pi$-$\pi^*$ electron transition of carbazole moiety. The first absorbance bands of FHCS and FBCS molecules showed strong absorbance band than NHCS and NBCS because of a nitro group more electron withdrawing nature compare to fluorine.

![Fig 2.34 TGA Curves of FHCS, FBCS, NHCS and NBCS](image-url)
The absorption bands of fluorine and nitro-molecules are almost identical. The FHCS and FBCS molecules showed maximum absorption peak at 390 nm and broad absorption band in the range of 300 nm to 420 nm. The NHCS and NBCS molecules are showed maximum absorption peak at 412 nm, the effect of nitro group increases the absorbance band up to 520 nm. The optical band gaps were calculated from UV absorption edge slope it was found to be 440, 441, 492 nm, and 492 nm. This results suggests optical band gap for FHCS, FBCS, NHCS and NBCS of 2.81, 2.81, 2.52 eV, and 2.52 eV, respectively. The PL emission peaks of FHCS, FBCS, NHCS, and NBCS in solution were observed at 458, 461, 543 nm, and 551 nm. The FHCS, FBCS, NHCS, and NBCS small molecules exhibited red emission with maxima at 543 and 551 nm, respectively.

The FHCS and FBCS small molecules showed weak fluorescence compare to NHCS and NBCS because of the fast-intramolecular charge transfer between donor (carbazole) and acceptor units. The nitro small molecules of NHCS and NBCS shift in 90 nm emission high compared to the fluorine-containing small molecule. It is recognized to the most extended conjugation of alternative carbazole-nitro phenyl acetonitrile segments and the strong donor–acceptor interaction. From the optical data of small molecules, the donor-acceptor interaction mainly depends upon donor-acceptor linkages, the strength of donor and acceptors, attachment of their backbones (Ahn et al., 2012; Baek et al., 2010).
2.7.4 ELECTROCHEMICAL PROPERTIES OF THE SMALL MOLECULES

The electrochemical properties were measured by cyclic voltammetry (CV) using platinum electrode in 0.1 M [Bu₄N][PF₆] acetonitrile solution at a potential scan rate of 500 mV s⁻¹. The CV spectra displayed in Fig 2.38, and corresponding data are summarized in Table 2.3. It is important to measure the HOMO and LUMO energy levels from oxidation potentials and reduction potentials. The onset oxidation potentials (E_{ox}^{onset}) were observed at 1.36, 0.89, 1.17 eV and 1.28
eV for FHCS, NHCS, FBCS and NBCS respectively. From the onset data, we calculate HOMO levels of -5.47, -5.28, -5.00 eV and -5.39 eV using the known equation \( \text{HOMO} = -eV (E_{\text{ox onset}} - E_{1/2 \text{ferrocene}} + 4.8) \).

![Cyclic Voltammograms of Small Molecules in CHCl₃ at a Scanning Rate of 500 mV s⁻¹](image)

**Fig 2.38** Cyclic Voltammograms of Small Molecules in CHCl₃ at a Scanning Rate of 500 mV s⁻¹

The LUMO energy levels of FHCS, NHCS, FBCS and NBCS were calculated from their onset reduction potentials \( (E_{\text{red onset}}) \) and found to be -0.80, -0.99, -1.08 eV and -1.18 eV respectively. The LUMO energy levels -3.31, -3.12, -3.03 eV and -2.93 eV were calculated using the known equation \( \text{LUMO} = -eV (E_{\text{red onset}} - E_{1/2 \text{ferrocene}} + 4.8) \). The band gap of the small molecules shows 2.16, 1.88, 2.25 eV, and 2.46 eV, respectively. It is close to P3HT and Fig 2.35, showed energy band gap diagram and all four small molecules suitable for organic solar cell applications.

**Table 2.3** Photophysical, Thermal Properties and Electrochemical Properties of Small Molecules

<table>
<thead>
<tr>
<th>Small molecules</th>
<th>Abs ( \lambda_{\text{max}} ) (nm)</th>
<th>( E_{\text{g opt}} ) (eV)</th>
<th>( T_d ) (°C)</th>
<th>( E_{\text{ox}} ) (V)</th>
<th>( E_{\text{red}} ) (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>( E_{\text{g}} ) (eV)</th>
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<tr>
<td>FHCS</td>
<td>326, 395</td>
<td>2.82</td>
<td>373</td>
<td>1.36</td>
<td>-0.807</td>
<td>-5.47</td>
<td>-3.31</td>
<td>2.16</td>
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<td>NHCS</td>
<td>336, 433</td>
<td>2.52</td>
<td>343</td>
<td>0.89</td>
<td>-0.99</td>
<td>-5.00</td>
<td>-3.12</td>
<td>1.88</td>
</tr>
<tr>
<td>FBCS</td>
<td>327, 396</td>
<td>2.80</td>
<td>359</td>
<td>1.17</td>
<td>-1.08</td>
<td>-5.28</td>
<td>-3.03</td>
<td>2.25</td>
</tr>
<tr>
<td>NBCS</td>
<td>341, 437</td>
<td>2.52</td>
<td>262</td>
<td>1.28</td>
<td>-1.18</td>
<td>-5.39</td>
<td>-2.93</td>
<td>2.46</td>
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</tbody>
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2.7.5 PHOTOVOLTAIC PROPERTIES OF THE SMALL MOLECULES

Organic bulk heterojunction solar cells were fabricated by using FHCS, NHCS, FBCS and NBCS as a donor material and PC$_{61}$BM as an acceptor material. The BHJ OSCs device fabrication is ITO/PEDOT:PSS/small molecules:PC$_{61}$BM/LiF/Al. The current–voltage (J–V) curves of the devices are shown in Fig 2.40, and their best device results are summarized in Table 2.4. The photovoltaic parameters of short circuit current (Jsc), open circuit voltage (Voc) and fill factor (FF) and PCE were observed maximum at (1:2, w/w) ratio for a donor:acceptor weight.
Although the \( \text{V}_{\text{OC}} \) is calculated from the energy difference between the HOMO energy level of the electron donor (small molecules) and the LUMO energy level of the electron acceptor (PC\(_{61}\)BM). The OSCs device based on NBCS:PC\(_{61}\)BM demonstrate the best performance, \( \text{Voc} \) of 0.75 V, \( \text{Jsc} \) of 4.35 mA cm\(^{-2} \), FF of 30.07% and PCE of 0.98%, respectively. The device based on NBCS exhibits a slightly higher \( \text{Jsc} \) and FF than that other small molecules because the NBCS having nitro and branched chain are enhanced this property. However, the device based NBCS and NHCS are exhibits a higher \( \text{Jsc} \) and FF values of 4.35, 3.90 mA cm\(^{-2} \), 30.07% and 29.76% respectively.

**Table 2.4 BHJ OSCs device performances of the small molecules:PC\(_{61}\)BM**

<table>
<thead>
<tr>
<th>Device</th>
<th>Donor:Acceptor</th>
<th>Ratio</th>
<th>( \text{Jsc} ) (mA/cm(^2))</th>
<th>( \text{Voc} ) (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FHCS:PCBM</td>
<td>1:2</td>
<td>2.02</td>
<td>0.75</td>
<td>26.10</td>
<td>0.40</td>
</tr>
<tr>
<td>2</td>
<td>FBCS:PCBM</td>
<td>1:2</td>
<td>2.72</td>
<td>0.76</td>
<td>27.54</td>
<td>0.57</td>
</tr>
<tr>
<td>3</td>
<td>NHCS:PCBM</td>
<td>1:2</td>
<td>3.90</td>
<td>0.77</td>
<td>29.76</td>
<td>0.90</td>
</tr>
<tr>
<td>4</td>
<td>NBCS:PCBM</td>
<td>1:2</td>
<td>4.35</td>
<td>0.75</td>
<td>30.07</td>
<td>0.98</td>
</tr>
</tbody>
</table>

**2.8 CONCLUSIONS**

We have successfully synthesized the new carbazole-based small molecules by easy step methods. In comparison with the fluorine and nitro small molecules, especially nitro-containing small molecules are showed broad absorption range, low band gap, and good thermal stability. The PL emission spectra showed the emission maxima at the same wavelength in both nitro and fluorine containing small molecules. The NHCS showed very low band gap of 1.88 eV compared to other due to its poor solubility its showed low performance in the device. The OSC device based on NBCS:PC\(_{61}\)BM demonstrate the best device performance, \( \text{Voc} \) of 0.75 V, \( \text{Jsc} \) of 4.35 mA cm\(^{-2} \), FF of 30.07 % and PCE of 0.98 %, respectively.