Chapter-3

3 Octadecylamine Functionalized SWNT doped Polymer Based Optoelectronic Devices

3.1 Introduction

3.1.1 Fundamentals of OLED

In recent years, there has been growing interest in organic (polymer) based optoelectronic devices such as organic solar cells, organic light emitting diodes (OLED), organic transistors, optical sensors, and photo detector[112][113][114]. OLED fabricate using polymer and small molecules because of their high brightness, wide viewing angle, ease of fabrication over large areas, low cost of manufacture, low power consumption, easy to fabricate on flexible substrates [115], light in weight and fast response time, they are ideal for a variety of applications [116][117]. OLEDs have garnered substantial interest for lightning and potential display applications. OLED displays are commercially accessible as television screens, media player displays, and smart phone displays [118]. Light emission from OLED depends on multiple layers such as hole injection layer (HIL), hole transport layer (HTL), emissive layer, electron transport layer (ETL) and electron injection layer (EIL)[119]. In multilayer OLEDs, the interface of the thin film layer and the characteristics of the materials have a significant impact on the injection and transport of holes and electrons. Excitation and recombination in the emissive layer are also affected by the manufacture process of OLEDs. Recent advances have been made in OLEDs' device structure, particularly their device interface [120].

3.1.2 Fundamentals of OLET

Recently another class of optoelectronic devices garnered substantial interest known as organic light emitting transistors (OLET). A type of multifunctional devices that a capacitor incorporate on the light source within conventional transistors, have been developed. Drain, active material, source, dielectric, and gate electrode are manufactured vertically in OLET also known as a vertical organic light emitting transistor (VOLET) [121]. Traditional horizontal structure transistors have limited current output even at high working voltages due to the lower electron and hole mobility of organic semiconducting materials [122]. VOLET's device construction consists of two cells, a capacitor and active or light-emitting cells connected by a common electrode [123]. Thin and porous middle electrode is the common-source electrode (S), which is a very important part of this device. The gate (G) and drain (D) electrodes are the top and bottom electrodes, respectively [124].

3.1.3 Charge transport materials for optoelectronic devices

OLEDs as well as VOLETs are less efficient due to unbalanced charge carriers induced by rapid hole mobility in the HTL and slow electron mobility in the ETL [125]. To optimise device performance, it is necessary to strike a balance between the injected charges and charge transport. The ideal material as HTL and ETL in organic devices has been the subject of extensive investigation. To effectively introduce holes from the anode, HTL materials must have a high work function. Organic semiconductor polymers are common HTL materials (PEDOT:PSS, TAPC, TCTA, CPB) [126][127]. Because of its excellent conductivity and optical transparency, PEDOT:PSS is among the most frequently utilized hole transport layers in organic devices [128]. ETL materials must have a low work function to provide a low barrier for electron injection from the cathode. ETL materials should also have excellent electron mobilities and chemical stability. ETL has been employed with a variety of organic molecules (CQDs, BCP, Alq_3, TPBI) and inorganic colloidal oxides nanocrystals (ZnO, TiO_2) [129][130]. To achieve high efficiency optoelectronic devices, the best HTL and ETL materials must be used.

3.1.4 Properties of SWNT

Carbon nanotubes (CNTs), especially single-walled carbon nanotubes (SWNTs), have garnered a great deal of interest due to their outstanding electrical, optical, and thermal capabilities, which make them suitable for optoelectronic devices [131]. Due to its ability to move charge carriers such as electrons and holes in optoelectronic devices, previous research has showed that CNTs can function as effective electrodes and hole transport layers in organic light-emitting diodes (OLEDs) and VOLETs [132][133]. SWNT is a transparent material with highly optical and electrical conducting properties[134]. Semiconducting SWNT possesses a wide tunable band gap and extremely high carrier mobility at room temperature working as a transparent semiconductor layer and as charge transporting layer.

In this chapter, we demonstrate octadecylamine functionalized single wall carbon nanotube (ODA-SWNT) doped into a PSBF film in a planar structure OLED as well as VOLET. The surface of the SWNTs was functionalized to increase their hydrophobicity while maintaining good dispersion in a solvent compatible with the organic polymer material, such as chlorobenzene [135]. Due to chemical functionalization of the surface of pristine nanotube, the electronic states were modified. The efficiency of the planar structured OLED comprising functionalized SWNTs was increased as compared to the device without SWNTs. Additionally we have also demonstrated VOLET, this important device exhibits two functions, generating light like an OLED and switching current like a transistor. Moreover, these optoelectronic device has an advantage in terms of fabrication because there is no damage to the organic layer as observed in electrode deposition using thermal evaporation.

3.2 Result and Discussion

3.2.1 Optical property of PSBF polymer and effect of doping with SWNT

The UV-vis spectrum of the polymer PSBF in DCB solution reveals an absorption maximum at 326, 399 and 435 nm and weak absorbance peak also observe at 377 nm. After the addition of SWNT (0.1 wt. %) in PSBF solution the peak position are same but peak intensity increases in uv-vis spectroscopy as shown in Figure *3.1* (a). Wang et al. discovered that the UV-vis spectra of PSBF polymers in toluene solutions exhibit two comparable absorption bands in the ranges 360-430 and 310-360 nm. The first absorption is caused by the polymeric backbone's π-π* transition, while the second absorption is caused by the spiro-conjugated system that exists between the backbone and the side fluorene and contains four alkoxyl groups [136].

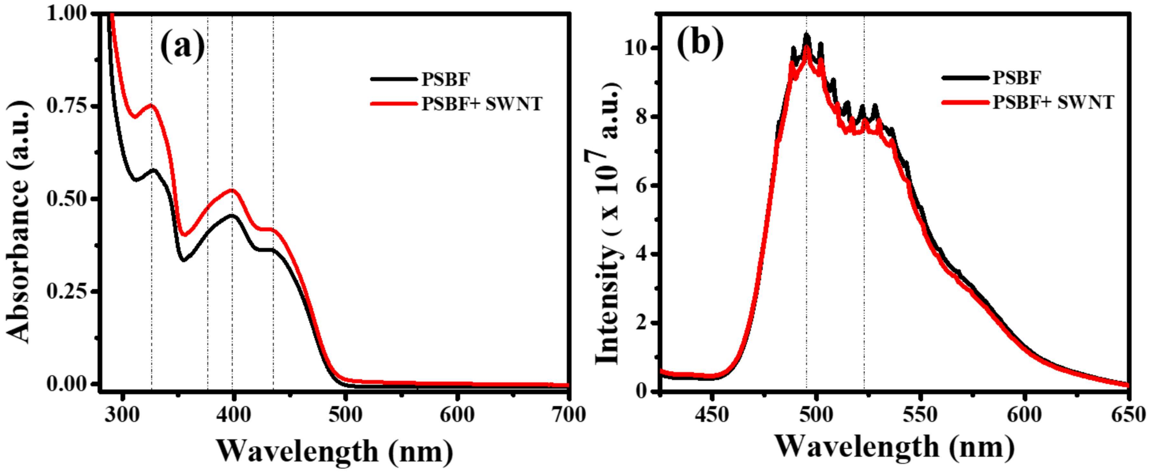

Figure 3.1 (a) UV-Vis absorption spectra of PSBF and doped with SWNT in DCB solution; (b) PL spectra of PSBF and doped with SWNT in DCB solution at 400 nm excitation wavelength.

The PSBF emission has two typical peaks at 495 nm, 523 nm, and one shoulder peak at 576 nm with the same excitation wavelength (λexc) at 400 nm. Here, the quenching effects shown by Adding SWNT (0.1 wt. %) on the PSBF solution are explored by comparison of the photoluminance (PL) intensities of PSBF solution with similar concentration as shown in Figure *3.1* (b). D. Marsitzky et. al. observed that the peaks of the fluorescence spectra of PSBF are positioned at 437, 464, and 495 nm, with two shoulders at 420 and 536 nm [137]. Numerous groups have reported the PL quenching of carbon-based nanomaterials such as CNT and graphene oxide (GO) [138]. Similar to prior study on SWNT, the PL quenching of PSBF by SWNT is caused by the photoinduced transfer of electrons from PSBF to SWNT. SWNTs display higher charge carrier mobility and serve as an exciton dissociation centre because to the 1-D transport channel. The PSBF-generated photoinduced excitons are dissociated at the SWNT interface and transmitted via the SWNT [139]. As a result, the exciton recombination is reduced, leading to a considerable reduction in PL.

3.2.2 Device structure of OLED

Figure *3.2* (a) is a schematic representation of the structure of OLEDs; the device structure is glass substrate ITO anode/PEDOT:PSS hole-transport layer (HTL)/PSBF emissive layer (EML)/SWNT electron transport layer (ETL)/LiF electron injection layer (EIL) (1 nm)/Al cathode (100 nm). The current versus voltage parameters of the energy band diagram of an OLED device with pristine PSBF and SWNT as ETL are depicted in Figure *3.2* (b).

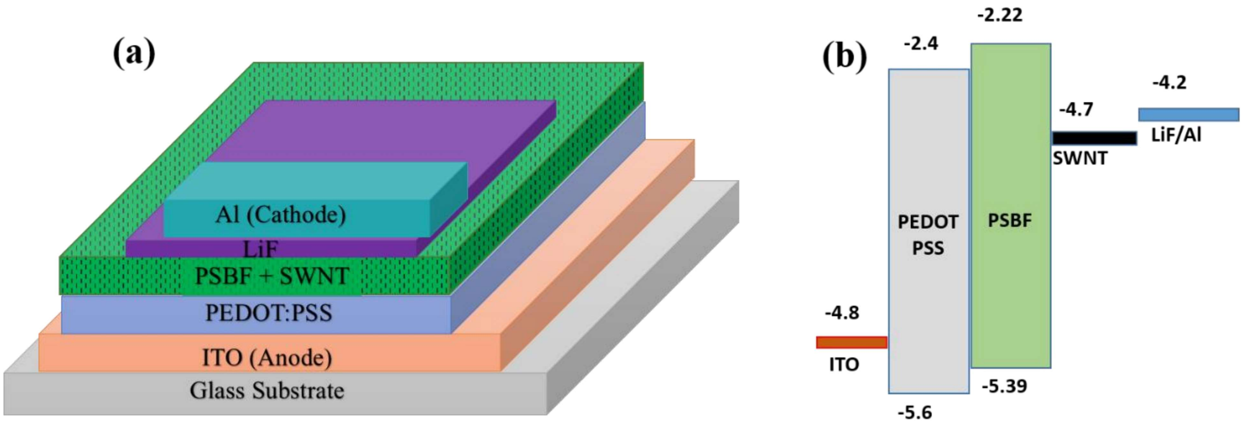

Figure 3.2 (a) Multilayer OLED device structure (b) Schematic representation of OLED energy level alignment

3.2.3 Doping Effect in OLED

Due to the doping of ODA-SWNT in OLED devices, the barrier height for electron injection is lowered, resulting in lower threshold voltages [140]. SWNT film has a work function of around 4.7 eV, which is too high to lower the energy barrier of electron injection from the cathode to the organic layers in devices. In order for the SWNT layer to be utilised as an effective cathode, its work function is modified by n-type doping during the transfer process. LiF 1 nm thin layer functions as EIL, the cut-off binding energy shifts by approximately 1 eV to higher binding energy, and the work function can be decreased to 3.2 eV or 3.3 eV using LiF layer utilising this transfer/doping procedure [141]. We've observed that compared to OLEDs without SWNT, OLEDs with SWNT are more stable and have a longer lifetime. Introducing SWNT as the ETL lowers the barrier for electron injection, hence decreasing the turn-on voltage. Electroluminescence (EL) comes from the recombination of electrons and holes in the active layer PSBF when subjected to under bias condition.

3.2.4 Electrical Characterization of OLED

Figure *3.4* (a) illustrates the current – voltage (I-V) characteristics of PSBF and PSBF doped with SWNT polymers. Compared to PSBF, the current in SWNT-doped PSBF appears to increase significantly at the same driving voltage. The LUMO levels of the polymers can be easily controlled to aid SWNT as electron transport layer, which results in the increased current. Due to the efficient recombination of electron and hole in OLEDs, the threshold voltage of SWNT-doped devices was dropped from 6 to 5V.

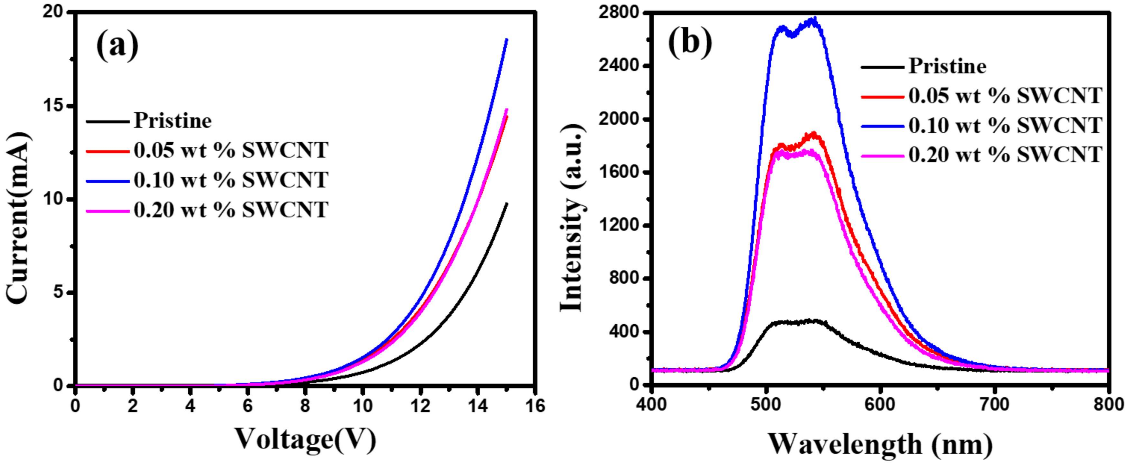

Figure 3.3 (a) Current voltage characteristics of OLEDs as function of operating voltage Pristine device and different weight % doped SWNT (b) Electroluminescence spectra of OLEDs operating voltage at 10 V Pristine device and various weight % doped SWNT

In addition, we took four devices, one of which was Pristine PSBF and the others were doped with SWNT at feed ratios of 0.05 wt %, 0.1 wt %, and 0.2 wt % (Figure *3.3* (a)). The threshold voltage decreased in all doped devices, but the threshold voltage obtained at 0.1 wt% was the lowest. In comparison to the other four devices, the EL intensity of the SWNT-doped 0.1 wt percent device at 10V is also quite high, as shown in Figure *3.3* (b). With the lowest threshold voltage and highest electroluminescence intensity, PSBF doped with SWNT (0.1% by weight) demonstrates the best device performance.

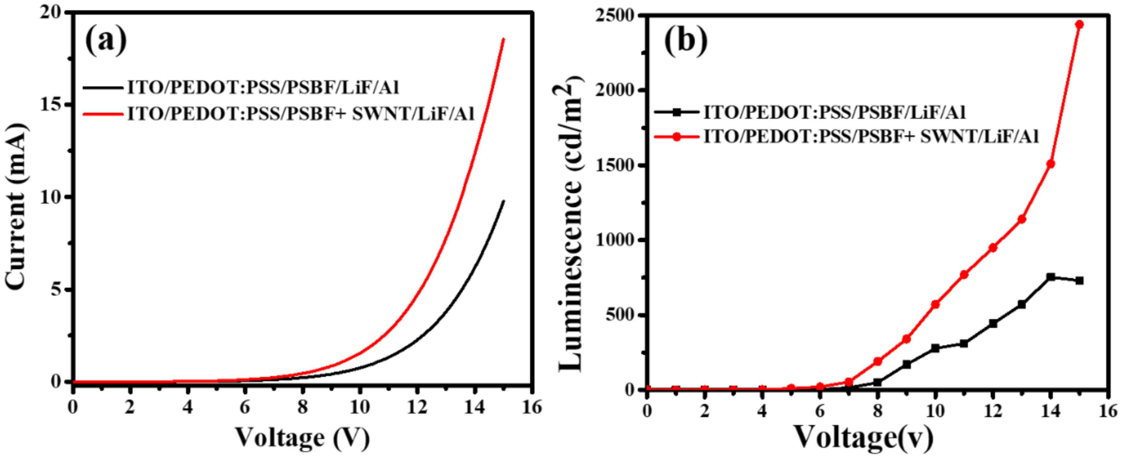

Figure 3.4 (a) I-V Characteristics of OLED (b) Luminescence Characteristics of OLED device structure ITO/PEDOT:PSS/PSBF/LiF/Al; ITO/PEDOT: PSS/PSBF+SWNT/LiF/Al

The luminescence - voltage characteristics of the polymers PSBF and PSBF doped with SWNT are illustrated in Figure *3.4* (b). When voltage is increased, OLED brightness increases. Both devices have the same features, however SWNT-doped devices are brighter than pristine devices. At 15 V, the luminescence intensity of the SWNT-doped device was many times higher than that of the pristine device.

Figure *3.5* (a) and (b) show the electroluminescence (EL) spectra of the Pristine PSBF device and PSBF doped with SWNT device depending upon operational voltages. The EL spectra for both devices exhibit strong peaks at 513 nm and 540 nm. In comparison to pristine devices, SWNT doped devices exhibit more strong EL peaks at the same working voltages. The intensity of the peaks grows proportionally with increasing voltage in both devices. However, at 11 V, the peak intensity of the SWNT doped device grows drastically, approaching saturation levels. These findings suggest that SWNT doped devices could be useful as electron transport layers in OLEDs.

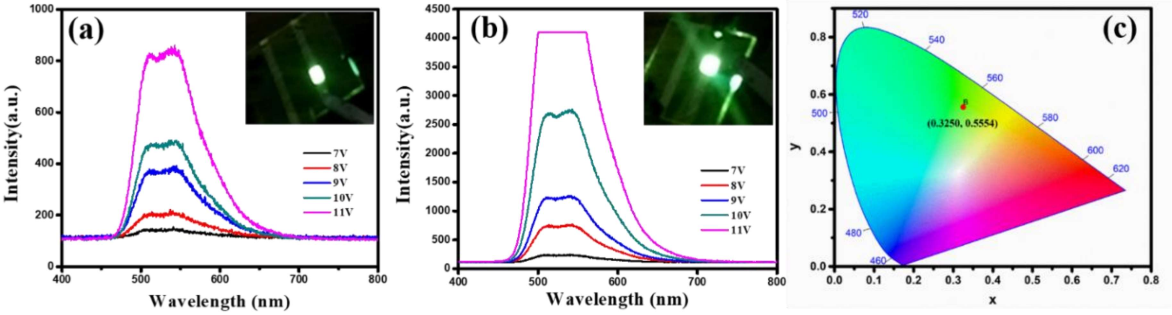

Figure 3.5 EL spectra of OLED depending on operational voltage (a) ITO/PEDOT:PSS/PSBF/LiF/Al (b) ITO/PEDOT:PSS/PSBF+SWNT/LiF/Al (inset shows brightness of OLED at 10 V) (c) CIE chromaticity diagram of the OLED devices

The CIE coordinates of the devices obtained from the EL spectra of Figure *3.5* (b) are displayed in Figure *3.5* (c). The emission peaks of green emitting diodes are 513 and 540 nm, and the CIE 1931 colour space chromaticity coordinates for green OLED devices are (0.32, 0.55). The CIE coordinates are positioned between the green colour of the diodes.

3.2.5 Device structure of VOLET

A vertical organic light-emitting transistor was demonstrated using the optimized VOLET device structure on glass substrate ITO drain /PEDOT:PSS (HTL)/PSBF (EML)/SWNT (ETL)/Al (porous source electrode 17 nm) /LiF dielectric material (100 nm)/Al gate (100 nm) as shown in Figure *3.6* (a). The turn-on voltage is similar to that of a standard OLED utilising the same light emitting polymer, but without the usage of a low work function electron injection layer like LiF. This finding indicates that using a porous source electrode lowers the VOLET's electron injection barrier. Compared to traditional optoelectronic devices with separate driving transistors, the VOLET device has several advantages, including intrinsically low power consumption, single stack device fabrication, and huge pixel aperture ratios.

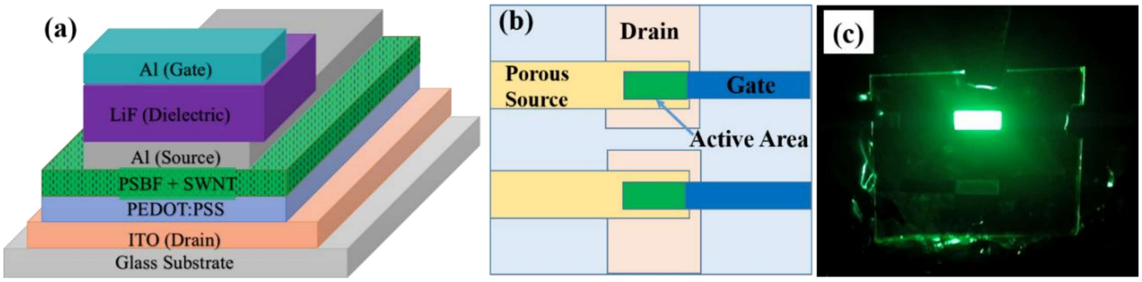

Figure 3.6 (a) Multilayer device architecture of VOLET fabrication (b) Schematic representation of VOLET's top perspective (c) Image of operational devices at V_{DS} = 10V and V_{GS} = 5V

The structure of a VOLET device, which is made up of an active cell and a capacitive cell. The traditional OLED structure of an active cell is formed by organic layers put between the drain (ITO) and source (Al) electrodes, and a capacitive cell is produced on top of the active cell. The heart of the device is a common porous source electrode that connects the active and capacitive cells. Figure *3.6* (b) provides an easy-to-understand top view of the structure of the device. The ITO drain should be the greatest from the bottom and the gate should be the smallest from the top, with the overlapping gate area representing the device's pixel. The VOLET device were investigated in ambient at room temperature and relative humidity of 38 percent utilizing Keithley 4200-SCS semiconductor characterization system with continuous sweep mode at varying applied gate voltages. The brightness of device were obtained with a digital camera as shown in Figure *3.6* (c).

3.2.6 Electrical Characterization of VOLET

Figure *3.8* (a) depicts the VOLET's output characteristics, at a constant drain to source voltage (V_{DS}), the drain current (I_D) increases as the gate to source voltage increases (V_{GS}). When the drain to source voltage is less than 2V, VOLET behaves like a transistor, with saturation currents in the order of μA, and when the voltage is greater than 2V, it behaves like an OLED full spectrum, as shown in Figure 3.7. When gate is positively biased in relation to the source, positive charge can form on the gate electrode surface and negative charge can form at the source–dielectric contact of a capacitive cell. Positive drain biasing causes holes to collect at the emissive layer (PSBF) interface and electrons to collect at the source-SWNT interface. As a result of electron and hole recombination at the PSBF–SWNT interface, an electric field may emerge, lowering the injection barrier at the PSBF source electrode interface. When the gate bias Vg is slightly higher than 1 V, light emission from the active layer can be seen. When the gate voltage is off Vg= 0V, because of the enormous injection barrier height between the Fermi level of the source electrode Porous Al and the LUMO of the emissive polymer. The electron current is very low, in this working condition, the electrons and holes are imbalanced. The energy level alignment between the source electrode and the organic material changes as the gate voltage is increased with the proper polarity, and the electron injection barrier is lowered. Even at low source-drain bias, higher and balanced electron-hole injection is achieved. As a result, excitons are created more efficiently in the emissive polymer, resulting in increased light emission.

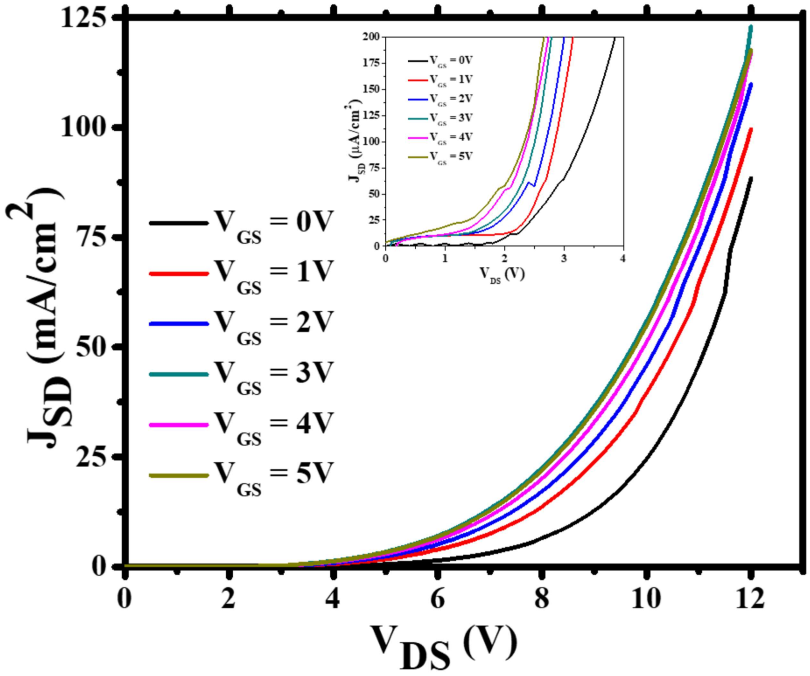

Figure 3.7 Full range of output characteristics of fabricated VOLET at different V_{GS} from 0 to 5 V

This electric field assists in the injection of electrons from the source electrode recombine with holes injected from the drain electrode at the emissive layer generate excitons in the form of light at the emissive layer. As demonstrated in Figure *3.6* (c), an increasing electric field causes enhanced electron injection from the source electrode to PSBF, which causes an increase in I_D. The barrier at this contact drops slightly as V_{GS} is increased to 5 V, allowing electron injection and resulting in green light emission.

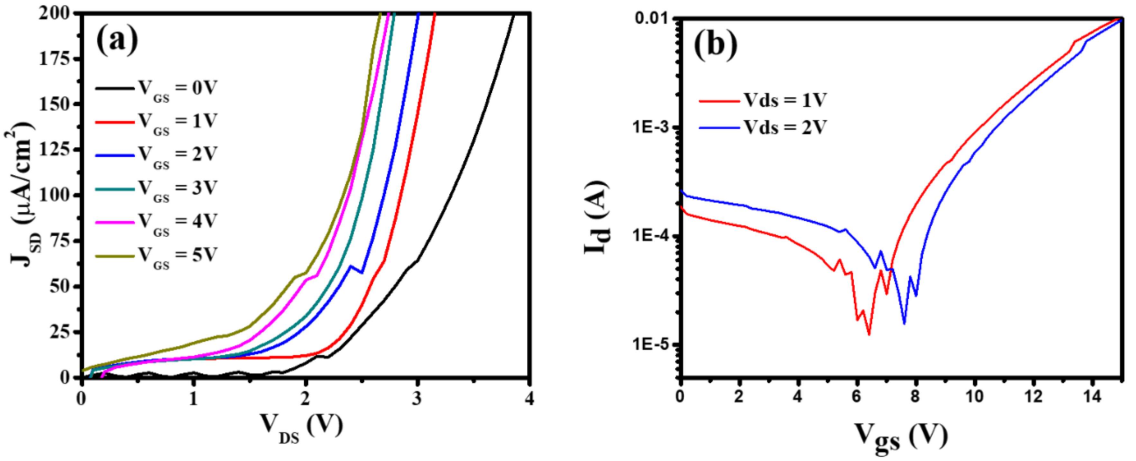

Figure 3.8 (a) Output characteristics of VOLET measured at varying V_{GS} values between 0 and 5 V (b) transfer characteristics of VOLET at varying V_{DS}

For proper device operation, thin, rough, and partially oxidized source electrodes must be fabricated [142]. The source electrode is rough and porous due to a thin covering, and aluminium oxide covers these pores. The created electric field formed in the capacitive cell may penetrate these pores and regulate electron injection when a gate electrode is subjected to a positive bias [143]. These pores are filled by growing Al when the source electrode thickness exceeds a particular threshold, preventing an electric field from reaching the source electrode and inhibiting the detection of the gate effect [144]. The VOLET's transfer characteristics are shown in Figure *3.8* (b). In comparison to 0 V to 15 V V_{GS} and 1, 2 V V_{DS}, the device achieves an ON–OFF ratio of greater than 10^3.

3.3 Conclusion

In conclusion, we have fabricated organic light emitting diode as well as vertical organic light emitting transistor. A PSBF hybrid structure with single-wall carbon nanotube (SWNT) doping has been successfully produced. The quantity of SWNT on the surface of the emissive polymer

PSBF can be easily adjusted. The brightness of the OLED increases due to SWNT doping, and the threshold voltage drops from 6V to 5V.

An electric field was formed in the capacitive cell of the VOLET when biasing was applied to all electrodes, and this induced electric field controls recombination and exciton generation in the active cell, thus controlling the current and emission intensity. Combining a phosphorescent OLED and a capacitor yields a vertical light-emitting transistor with an ON/OFF brightness ratio greater than 10^3. The device has transistor characteristics up to a functional drain-to-source voltage of 2V, but when the voltage exceeds 2V, it transforms into an OLED. The VOLET will become a universal device platform for creating numerous optoelectronic sensors or photodetector units in the future due to the use of the ITO electrode, which has been a common bottom electrode for many optoelectronic devices. With their great performance parameter, fabricated OLEDs and VOLETs bring up new options for future organic material devices.