Study of Narrow Energy Band Gap Polymer Matrix for Organic Field-Effect Transistor-based Biosensor

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Abstract

In this project, triisopropylsilylethynyl-pentacene (TIPS-pentacene) will be utilized as a semiconducting polymer matrix for the preparation of biosensors based on organic field-effect transistor (OFET) structure. A thin layer of TIPS-pentacene can be easily formed on a silicon substrate through solution processable technique. Through polymer blend method which allows synergistic combinations of stacking configurations of multiple polymers energy levels which will enhance overall charge transport. Novel pentacene derivatives will also be proposed using machine learning method and computational study for synthesizing new narrow energy band gap polymer matrix. Analytical techniques, such as ultraviolet-visible (UV-Vis) spectroscopy will be used in the characterization of the materials properties. The proposed biosensor based on integration of biological compound into OFET will facilitate the government.

Keywords: *Triisopropylsilylethynyl-pentacene; organic field-effect transistor; semiconducting polymer matrix; biosensor.*

1.0 Introduction

Previous research has demonstrated the potential of OFET-based biosensors for detecting the various disease by the presence and amount of biological compound [1,2,3]. But, due to lack of charge mobility, stability and reproducibility, OFET devices eventually has limitation to their performance and affect sensor detection [4,5]. Moreover, further research is needed to maximize its practicality for the use in medical environments. There are several strategies to improve the functionality of OFET to detect infectious diseases more accurate. One of the methods is via blend strategy [6]. The electrical performance of an OFET device with common material such as pentacene for instance which can be enhanced by blending with other semiconductor materials whether small molecules or polymers [7].

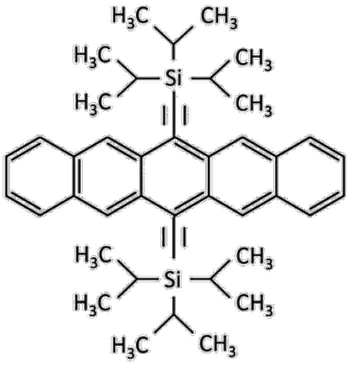


Fig. 1. TIPS-pentacene molecular structure

In this project, 6,13-bis(triisopropylsilylethynyl)pentacene or TIPS-pentacene will act as polymer matrix for the preparation of OFET-based biosensor. It was selected as a main polymer matric due to its excellent solubility in many organic solvents, make it easier to be utilized in many solution-process methods for large area and low-cost electronic devices [8,9,10,11]. As Fig.1 shows the molecular structure of TIPS-pentacene, it also can use the same solvent that be dissolved by other semiconductor materials, it can mix and allows its electrical parameter such as energy band gap to be tuned [12,13,14,15]. It is expected that by reducing the energy band gap, it can help to increase the mobility [16,17].

A composite can be obtained by blending two different conjugated polymers with different band gaps and tunable band gap could be adjusted by changing the blending ratio of the two polymers. The best methods for tuning the band gap of OFETs is by interpenetrating polymer networks and polymer blending which allowing for the control of the band gap and the improvement device performance [18,19,20,21]. Furthermore, TIPS-pentacene also have the highest hole mobility at the room temperature that made an optimum option among the organic materials and polycrystalline. Its application is much as like Polyacene and Anthracene single crystals and thin films of Tetracene, Anthracene as well as thin film structures are also investigated. The latest material including P3HT poly (3-hexylthiophene), TIPS-pentacene are P-type because the contact metal Fermi level is very close to the highest occupied molecular orbital (HOMO) level instead of lowest unoccupied molecular orbital level (LUMO): hence on the basis of this the P-type semiconducting materials are well developed and more stable in atmosphere than the N-type materials.
Moreover, a high annealing process is required to prepare materials with a high dielectric constant, which is impossible in plastic. Several applications use organic field-effect transistors (OFETs), which are active layers in matrix displays, biological sensing, chemicals, radio frequency identification (RFID) tags, and flexible electronics [22].

2.0 Methodology

2.1. Synthesis of narrow the energy band gap of pentacene derivatives

A conjugated polymer, TIPS-pentacene, was dissolved using two different solvents, namely chloroform and dimethylformamide (DMF). Both solutions were constantly stirred for 1 hour using magnetic stirring to obtain a uniform solution. In this process, there were only two reference samples on two different substrates. The samples were run under UV-Vis. A new solution of co-polymer materials was prepared for creating interpenetrating polymer networks (IPN).

2.2. Fabrication of organic field-effect transistor

The ITO glass substrate was used for OFET and Sensing as shown in Fig. 2, which has been designed to enable the fabrication and characterization of transistors and sensing devices without the need for vacuum evaporations or probe stations. This is to make a system ideal for reducing the costs of material screening experiments, but allows devices to be produced and tested with significantly increased simplicity.

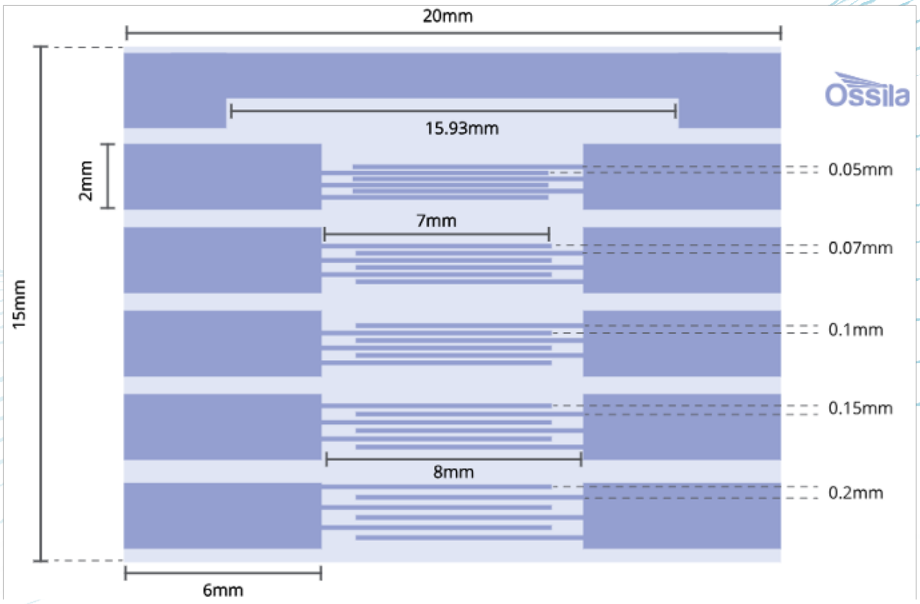


Fig. 2. Ossila ITO OFET substrate variable schematic. The Gate channel length is 20mm. The Drain and Source channel lengths are 6mm and 8mm apart from each other

By simply depositing an organic semiconductor, gate insulator, and gate on the substrates, the transistor can be fabricated. By using a synthetic metal such as PEDOT; PSS, deposited from solution for the gate, it is possible to make a fully functioning OFET with solution processing alone, eliminating vacuum evaporation processes. The substrates were also designed to work with a wide variety of different material systems and deposition techniques, while all solution-based processing allows transistors to be fabricated in a matter of minutes.

2.3. Optimization of biosensor

By using a combination of other polymer materials, it can achieve optimized interpenetrating polymer networks (IPN). The TIPS pentacene will be added to this co-polymer solution to tune its energy band gap. The same process of phase 2 was used to fabricate the same OFET sensor devices but with a different combination of co-polymer IPN. The process will be continued to optimize the OFET sensor by fabricating the same OFET biosensor devices on the ITO-coated PET film with pre-patterned source-drain channels. The pre-patterned source-drain channels are formed using the photolithography technique before the deposition of the mixed TIPS pentacene and co-polymer solution. These OFET biosensors will also be characterized using SMU to obtain current-voltage characteristics for saturation and transfer curves.

2.4. Collecting real data and analyze

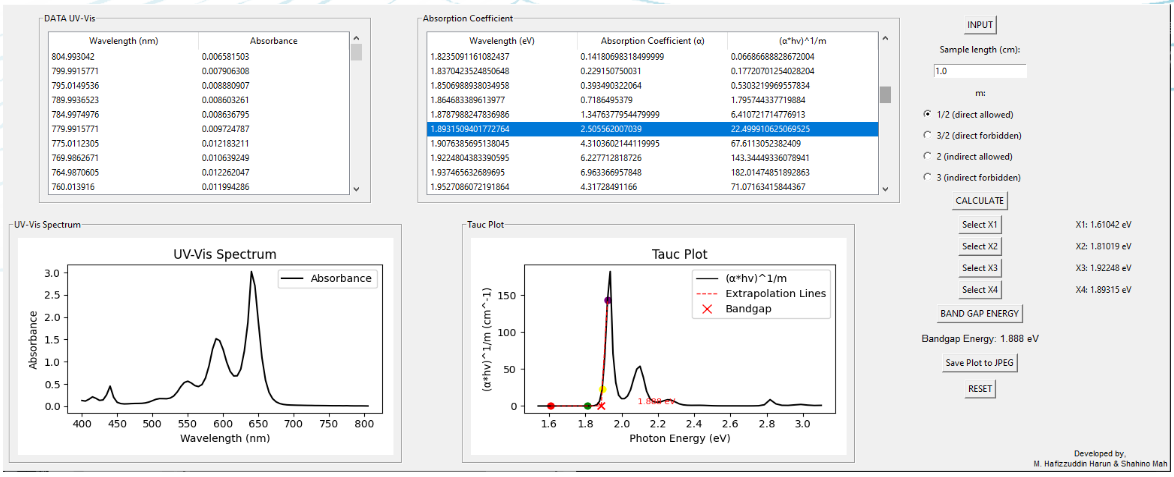
The fabricated organic field-effect transistor (OFET) biosensor was connected to a microcontroller unit (MCU) and an Analog Devices M1K ADALM1000, which were used to collect data based on changes in electrical signals when the sensor detected the presence of a target substance. The acquired data were analyzed using the Tauc plot method to determine the optical band gap energy (Eg). The optical band gap energy (Eg) of a semiconductor was a crucial parameter that defined the minimum photon energy required to excite an electron from the valence band to the conduction band [23]. According to Eq. (1), the optical absorption coefficient (α) of a semiconductor was energy-dependent and followed the relation:

$$(ahv)^{\frac{1}{n}} = A\,(hv - Eg) \tag{1}$$

where h is the Planck constant, ν is photon's frequency, Eg is bandgap energy, C is a constant, and α is the absorption coefficient which describes how much light of a given colour is absorbed by a material of given thickness. Depends on the nature of electron transition, the n is numerically equal to o 1/2, 3/2, 2 or 3 for direct allowed, direct forbidden, indirect allowed, or indirect forbidden transitions, respectively. By analysing the Tauc plot, we can gain deeper insights into the electronic and optical properties of the semiconductor material used in the biosensor.

3.0 Results and discussion

The electrical properties of an organic semiconductor are studied to measure the current-voltage characteristics. The main electrical characteristics in the organic field-effect transistor is determined by the charge carrier transport in the polymer material across a gap between the Source and Drain terminals. The terminal that majority charge carrier enter the FET is called Source, while the terminal that majority charge carrier exit the FET is called Drain. The charger carrier mobility in polymer are limited to hopping mechanisms across the band gap between the interfaces of Source/conjugated molecules/Drain. The result is obtained from the UV-vis spectroscopy which can calculate material's light absorption in solution form.



DATA UV-Vis

Wavelength (nm)	Absorbance
804.993042	0.006581503
799.9915771	0.007906308
795.0149536	0.008880907
789.9936523	0.008603261
784.9974976	0.008636795
779.9915771	0.009724787
775.0112305	0.012183211
769.9862671	0.010639249
764.9870605	0.012262047
760.013916	0.011994286

Absorption Coefficient

Wavelength (eV)	Absorption Coefficient (α)	(α*hv)^1/m
1.8235091161082437	0.14180698318499999	0.06686688828672004
1.8370423524850648	0.229150750031	0.17720701254028204
1.8506988938034958	0.393490322064	0.5303219969557834
1.864683389613977	0.7186495379	1.795744337719884
1.8787988247836986	1.3476377954479999	6.410721714776913
1.8931509401772764	2.505562007039	22.499910625069525
1.9076385695138045	4.3103602144119995	67.6113052382409
1.9224804383390595	6.227712818726	143.34449336078941
1.937465632689695	6.963366957848	182.01474851892863
1.9527086072191864	4.31728491166	71.07163415844367

Sample length (cm): 1.0

m:
● 1/2 (direct allowed)
○ 3/2 (direct forbidden)
○ 2 (indirect allowed)
○ 3 (indirect forbidden)

X1: 1.61042 eV
X2: 1.81019 eV
X3: 1.92248 eV
X4: 1.89315 eV

Bandgap Energy: 1.888 eV

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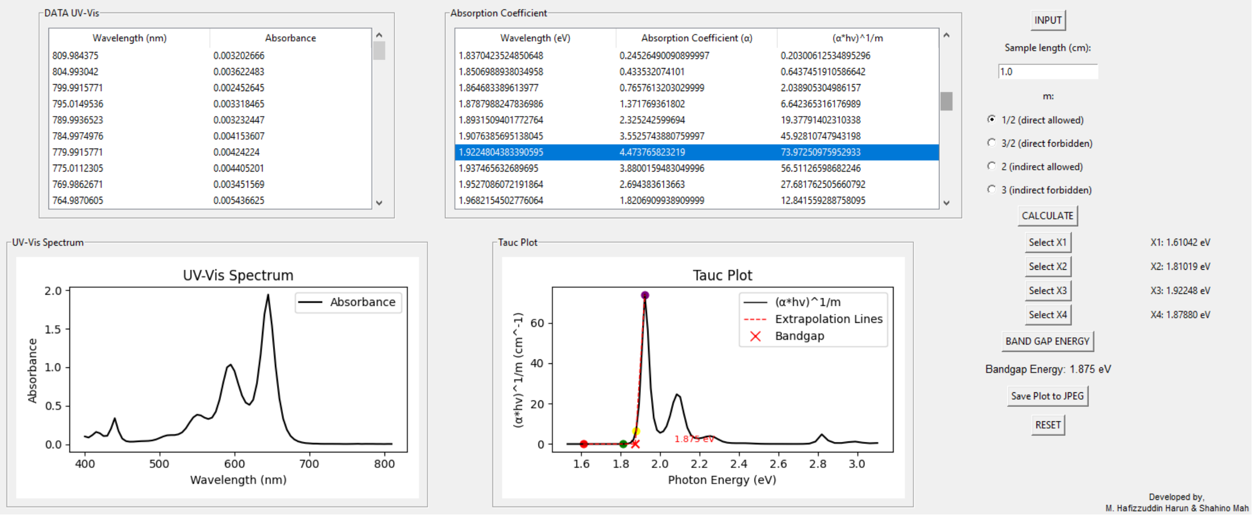
Fig. 3. The plotted graph of TIPS-pentacene solvent with chloroform



DATA UV-Vis

Wavelength (nm)	Absorbance
809.984375	0.003202666
804.993042	0.003622483
799.9915771	0.002452645
795.0149536	0.003318465
789.9936523	0.003232447
784.9974976	0.004153607
779.9915771	0.00424224
775.0112305	0.004405201
769.9862671	0.003451569
764.9870605	0.005436625

Absorption Coefficient

Wavelength (eV)	Absorption Coefficient (α)	(α*hv)^1/m
1.8370423524850648	0.24526490090899997	0.20300612534895296
1.8506988938034958	0.433532074101	0.6437451910586642
1.864683389613977	0.7657613203029999	2.038905304986157
1.8787988247836986	1.371769361802	6.642365316176989
1.8931509401772764	2.325242599694	19.37791402310338
1.9076385695138045	3.5525743880759997	45.92810747943198
1.9224804383390595	4.473765823219	73.97250975952933
1.937465632689695	3.8800159483049996	56.51126598682246
1.9527086072191864	2.694383613663	27.681762505660792
1.9682154502776064	1.8206909938909999	12.841559288758095

Sample length (cm): 1.0

m:
● 1/2 (direct allowed)
○ 3/2 (direct forbidden)
○ 2 (indirect allowed)
○ 3 (indirect forbidden)

X1: 1.61042 eV
X2: 1.81019 eV
X3: 1.92248 eV
X4: 1.87880 eV

Bandgap Energy: 1.875 eV

Developed by,
M. Hafizzuddin Harun & Shahino Mah

Fig. 4. The plotted graph of TIPS-pentacene solvent with dimethylformamide

From Fig.3, the data were inserted into a software, and it calculates the energy band gap. The Tauc Plot is used to determine the optical bandgap of either disordered or amorphous semiconductors. The optical band gap of TIPS-pentacene, ranging from 1.6 eV to 1.87 eV in thin film form, is commonly reported to be around 1.72 eV. In this work, the value of the optical bandgap was found to be 1.888 eV when dissolved in chloroform. While for the UV-vis spectrum shows the absorbance vs wavelength (nm). The curve for this graph is the same curve of blue colour wavelength, which peaks between 600 nm to 700 nm. Then, for Fig.4, the value of bandgap energy obtained was 1.875 eV when dissolved in DMF. While for the UV-vis spectrum shows the same curve as Fig.3, which is a peak between 600 nm to 700 nm. The reason both consist of the same UV-vis spectrum curve is that each solution is a dye in blue colour.

The difference between the optical bandgap energies of TIPS-pentacene dissolved with chloroform (1.888 eV) and dimethylformamide (1.875 eV), observed as such, is due to the influence of the solvent and not measurement error. This is because all the experimental conditions, like polymer concentration, stirring rate, substrate type, sample preparation, and measurement configurations, remained consistent to eliminate variability. Further, the readings were consistent with replicable values being taken from repeated experimentation, indicative of systematic rather than random error. Even the small variance of 0.013 eV, although small, lies outside the normal error range for UV-Vis spectroscopy and must therefore be considered significant. The deviation can be accounted for by the differing interactions of the solvents with the TIPS-pentacene molecules. The non-polar solvent chloroform and the polar solvent dimethylformamide (DMF) influence the molecular conformation of the polymer, chain packing, and film morphology in various ways when dissolving and casting into films. The electronic structure, particularly the π-π stacking, is influenced by these alterations, inducing slight alterations in the optical bandgap. Parallel solvent-dependent behaviour was shown by conjugated polymers according to the literature, so the conclusion based on this that the observed difference is due to solvent effect rather than instrumental or reading error is supported further.

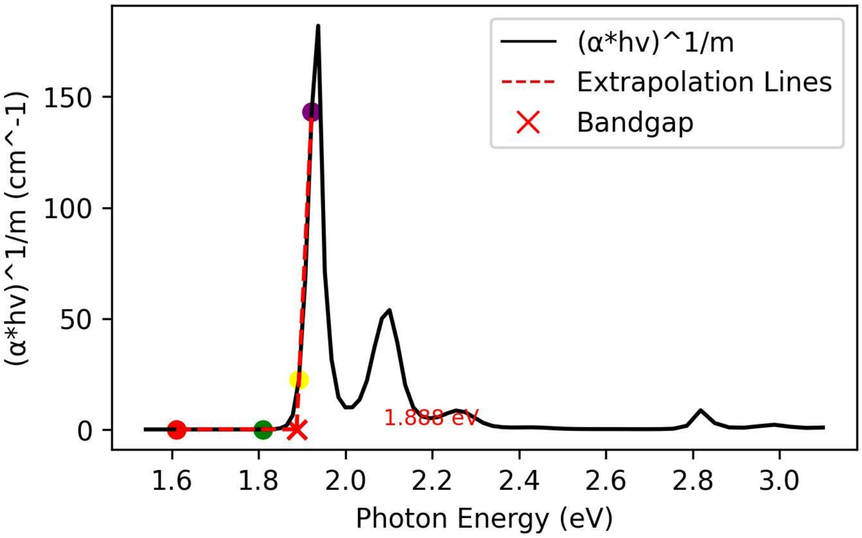


Fig. 5. Tauc Plot of TIPS-pentacene diluted with chloroform

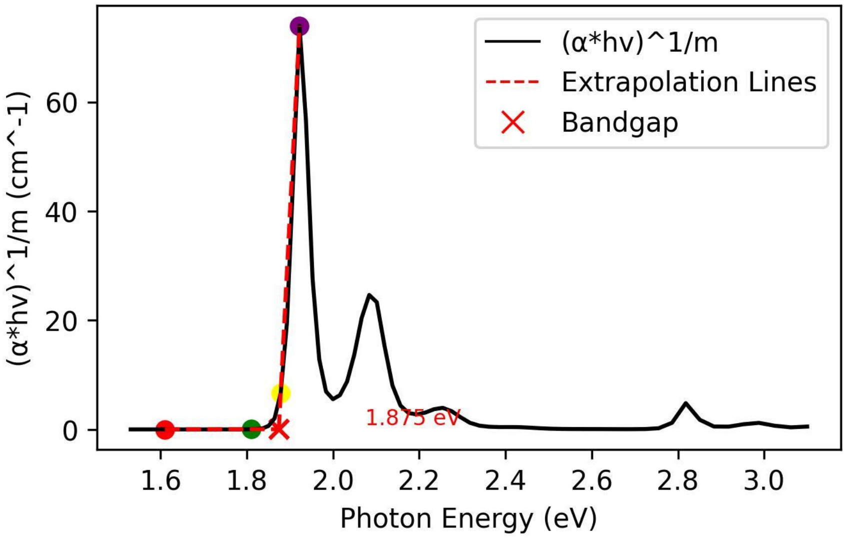


Fig. 6. Tauc Plot of TIPS-pentacene diluted with dimethylformamide

4.0 Conclusion

The solution of TIPS-Pentacene dissolved in both DMF and chloroform has been prepared to determine the optical energy band gap. This measure will be very helpful for the fabrication of OFET-based biosensors. By comparing the results between two solvents, DMF has a slightly better, negligible bandgap energy, which is 1.875 eV, while for the solvent chloroform, it is 1.888 eV. The bandgap energy represents the minimum energy that is required to excite an electron up to a state in the conduction band where it can participate in conduction [25]. The solvents that have higher boiling points result in larger grain size and can improve crystallinity [26]. By combining both lower bandgap blended polymer matrix and an increase in Gate applied voltage which make detection rate will significantly increase. A decrease in bandgap in a polymer material means a lower amount of energy required to excite electrons from the valence band to the conduction band, so more charge carrier generation occurs upon light or analyte exposure. Enhanced carrier density enhances the conductivity and sensitivity of the organic field-effect transistor (OFET) channel. It can be a potential candidate for the biomedical sensor to rapidly detect infectious diseases because of has better internal charge carriers. When rapid and accurate detection of the disease can be carried out within a short time, it can provide immediate information to curb the spread of infection and save more lives.

Acknowledgements

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