

Optical Characteristics of ITO/NTCDA Film for Defence Technology Application

Nursaadah Ahmad POAD^{1,a}, Siti Zulaikha Ngah DEMON^{2,b*}, Muhd Zuazhan YAHYA^{1,c} and Noriah BIDIN^{3,d}

¹Fakulti Sains dan Teknologi Pertahanan, Universiti Pertahanan Nasional Malaysia, Kem Sungai Besi, 57000 Kuala Lumpur, MALAYSIA.

²Pusat Asasi Pertahanan, Universiti Pertahanan Nasional Malaysia, Kem Sungai Besi, 57000 Kuala Lumpur, MALAYSIA.

³Laser Center, Universiti Teknologi Malaysia, 83100 Johor Bharu, MALAYSIA

^anursaadah_ahmadpoad@yahoo.com, ^bzulaikha@upnm.edu.my, ^cmzay@upnm.edu.my, ^dnoriah@utm.my

ABSTRACT. The interface structure between inorganic/organic layer governed microscopic and physical property of many organic based devices. The 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) is strong electron acceptor and its thermal stability can be explored in electro-optics application and laser material. In this study, optical characteristics of NTCDA film at interface of indium tin oxide (ITO) was demonstrated. The film was processed using ethanol and toluene solvents at 1:1 ratio before spin coated on 180 nm thickness ITO substrate. Hexamethyldisilazane (HMDS) was used to surface functionalized the ITO substrate. Analysis of AFM images showed the NTCDA film grown on ITO substrate at grain size approximately 0.5-1.5 μm . The onset of the absorption band shifted around 0.11 eV upon HMDS modification at interface of NTCDA film and ITO substrate indicating electronic modification on the bulk NTCDA film. Structural conformation was studied using the infrared absorption. Other than strong absorption peak at 1783 cm^{-1} that belonged to vibrational mode of the C = O functional group of the NTCDA, the fingerprint peaks of NTCDA on FTIR spectra were present with or without HMDS modification. This study showed the bandgap tuning of organic semiconductor film using surface functionalization technique as potential material processing in defence technology application.

Keywords: Organic semiconductor, Surface functionalization, Spin coating, Optical characteristic;

Received: 15.10.2017, **Revised:** 15.12.2017, **Accepted:** 30.02.2018, and **Online:** 20.03.2018;

DOI: 10.30967/ijcrset.1.S1.2018.262-268

Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia.

1. INTRODUCTION

Since the last decade, thin films of molecular organic semiconductors are attracting much interest for electronic and optoelectronic applications [1]. Technologies such as organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs) and organic field-effect transistors (OFETs) have been steadily evolving and penetrating the mainstream consumer electronics market [2-3]. Organic device is more preferable because of easy fabrication. For example, OFETs can be manufactured near room temperature on plastic and rubber. This temperature is not possible for silicon-based device [4]. Solution processing are also possible in wide range of organic materials. This technique has the advantageous to be applied in existing thin-film coating technologies from inkjet and screen printing for individual substrates to continuous roll-to-roll manufacturing using slot-die coating, gravure printing or doctor-blading [5]. Other than potential

applications as flexible displays, RF-ID components and e-papers, the organic semiconducting materials had been explored for photonics, electro-optics and laser materials [6-7]. The material can be fabricated into eyes protection devices and sensors for intense laser beams that is useful in military and weaponry purpose [6]. Styrylbenzene derivatives luminescent material is candidate laser active materials [7]. Lasing threshold was reduced by controlling the bandgap of small molecular materials and conjugated polymers [7].

Organic semiconductor molecule, 1,4,5,8-naphthalene-tetracarboxylic dianhydride, $C_{14}H_4O_6$ (NTCDA) is a prototype π -conjugated molecule that has been investigated in both experiments and theories [8]. Previous researches found that compounds containing six-membered imide rings have possible application in optoelectronics and photonic technology [9]. One advantage of NTCDA is its thermal stability that allows thermal treatment up to ~ 450 °C without chemical or physical decomposition [10]. The intermolecular interaction between NTCDA molecule and various surfaces such as Au, Ag and Al had been widely investigated. A study by Tonner et al showed the NTCDA monolayers interacts with substrate Ag(111) via non-directional van der Waals forces and covalent bonding of the acyl oxygen atoms with underlying Ag atoms [11]. The information was extracted using the infrared absorption data.

For devices, there is not only physical but electronic barriers exist at interfaces between dissimilar material such as between inorganics and organics, ITO is included [12]. The indium tin oxide (ITO) is n-type semiconductor with bandgap of ~ 4 eV. In order to overcome the barrier, interactions at the interface can be modified so that desired electronic property such as electronic bandgap can be realized. One way is to attach a functional organic on the electrode surface such as hexamethyldisilazane (HMDS). The HMDS is a self-assembled monolayers (SAMs) [13]. HMDS is safe and non-corrosive, therefore, it have been used widely as photoresist adhesion-promoting agent [14]. HMDS also will produced lower porosity on film grown with it. The HMDS treatment at interface of substrate and organic film not only improve the quality of the organic semiconductor film but also increase charge carrier density by decreasing the interface trap density . Investigation done by Fiorillo et al showed the surface of Si substrate becomes silated and non-polar surface upon treatment of HMDS. It was found to reduce surface energy of Si substrate [13].

In this study, the organic film were fabricated by solution-processed method using spin coater. Spin-coating technique is easy, versatile, inexpensive and highly effective for depositing uniform thin film reproducibly. This fabrication method is convenient for rapid device testing purpose. The film thickness can varied from 20 – 200 nm. Previous study shows electrical performance of spin coated OFET strongly correlated with the morphology and solid-state order of the deposited semiconductor layer [14]. Here, the solution was spin-coated on indium tin oxide (ITO) substrate of organic field-effect transistor (OFET) following solution deposition of HMDS. Optical characterization on spin coated NTCDA film reported in this paper is a part of initial procedure preceding the investigation of the film property at nanoscale.

2. MATERIALS AND METHODS

The processing of organic semiconductor solution was produced under atmospheric condition. Here, 0.08 wt.% of NTCDA in powder form (95%, Sigma Aldrich) was dissolved in 1:1 ethanol and toluene solvent [9]. Hexamethyldisilazane, HMDS (95%, Sigma Aldrich) was used as received. The brown powder of NTCDA did not immediately dissolved in the solvents but the aggregates slowly disappeared after continuous stirring at constant temperature of 100 °C. Fig. 1 shows the transformation of NTCDA aggregates in this processing condition. At 120 H stirring, the aggregates size distribution varied from 1 μm to 20 μm . The aggregates can be origin of many linear and non-linear optical phenomenon. The final solution was taken when the aggregates were no longer visible under observation of 10 \times magnification optical microscope as shown in Fig. 1 (b). The organic films were spin coated at low speed frequency of 500 rpm. The ITO substrates were cleaned with acetone and isopropanol prior film deposition. HMDS were spin-coated on ITO to form uniform

monolayer on the substrate. Finally, the films were dried at 25 °C and later 120 °C to allow solvent evaporation. The thickness of spin coated NTCDA film was determined by Atomic Force Microscope (AFM). Optical characterization of NTCDA solution was done by UV-Vis spectrometer (Genesys ^{TM6}, Thermo Scientific) while morphology of NTCDA thin film were characterized by using optical microscope, UV-Vis-NIR (Lambda 950, Perkin Elmer), and Fourier transform infrared spectroscopy (FTIR).



Fig. 1 The photomicrogram of NTCDA film after (a) 120 H, (b) 240 H of continuous stirring at temperature 100 °C. The images were taken under 10x magnification and (c) Sample structure of glass/ITO thin film/NTCDA film. The HMDS are deposited as SAMs between the electrode and organic layer

3. RESULTS AND DISCUSSION

The surface area of polycrystalline ITO thin film was scanned using AFM. The thickness of the thin film is 180 nm, a typical thickness for anode of OLED. The bare ITO are homogenous film with surface roughness up to 30 nm. The average grain size of the ITO was determined to be 0.2 μm as shown in 5 μm × 5 μm AFM image below (Fig. 2(a)). Meanwhile, Fig. 2 (b) shows a new surface image obtained after deposition of NTCDA film. This film was deposited with HMDS treatment on the ITO surface. The analysis on the 10 μm × 10 μm surface shows the roughness of the film is approximately ~200 nm with grain size of 0.5-1.5 μm. The roughness of the surface was determined using the difference between the highest and lowest point of the film thickness. The NTCDA film produced from this processing condition was not homogenous as well as having large grain and this usually leads to short-circuit in devices.

The thickness of the organic film was determined using the line scan of 10 μm × 25 μm surface image (Fig. 2 (c)). It can be estimated from the line profile that film thickness is approximately ~125 nm thick. The top line profile belonged to Line A on the image of NTCDA film. It can be seen that the film grew thicker toward the film's edge. Line B contained the surface roughness information both the film and the substrate. Because the film did not cover the whole surface area of the ITO, the surface becomes really rough. In the microscopic point of view, the NTCDA molecules may not form good intermolecular interaction with the ITO's surface. This type of non-uniformity at the interface can damage the organic device. On the other hand, the organic semiconductor molecules is known to stack vertically in crystalline manner due to non-covalent π-π stacking interactions provided by the aromatic rings of NTCDA [12]. The information on the crystalline stacking could only be confirmed using XRD or FESEM measurement.

In Fig. 3, three UV-Vis absorption spectra were used to study electronic structure of single layer NTCDA film (Spectrum A), NTCDA solution (Spectrum B) and HMDS surface modified NTCDA film (Spectrum C). The UV-Vis-NIR measurement of the films were taken with ITO substrate as reference, thus optical property of the ITO became negligible. Spectra comparison is made in order to check the electronic modification after the NTCDA solution is deposited as film as shown in Fig. 3(a). Since the absorption spectrum indicates molecular electronic transition, the onset of absorption is considered as gap of semiconductor. In the visible light region, the absorption edge of both spectra overlapped at 3.1 eV indicating no electronic change in the NTCDA film. This finding is true for bulk NTCDA as the compound is stable in both solution and solid state. However, there were noticeable absorption at 400 nm-600 nm in Spectrum B originated from the film thickness. Meanwhile, Spectrum C was obtained from the NTCDA film fabricated on surface functionalized ITO. From the

comparison at the absorption edge in Fig. 3 (b), there exist a small shift ~ 0.11 eV of electron energy. This change of optical characteristics may indicated electronic modification of bulk film originated by improved molecular order at the interface. The bathochromic shift was also seen in P3HT:PCBM thin film due to conformational order in macroscopic scale that result into different energy level distribution. The modification at the surface using HMDS had caused the collection of the irradiation to be broadened and difference in HOMO and LUMO levels to be smaller, thus lowering the bandgap of the NTCDA film.

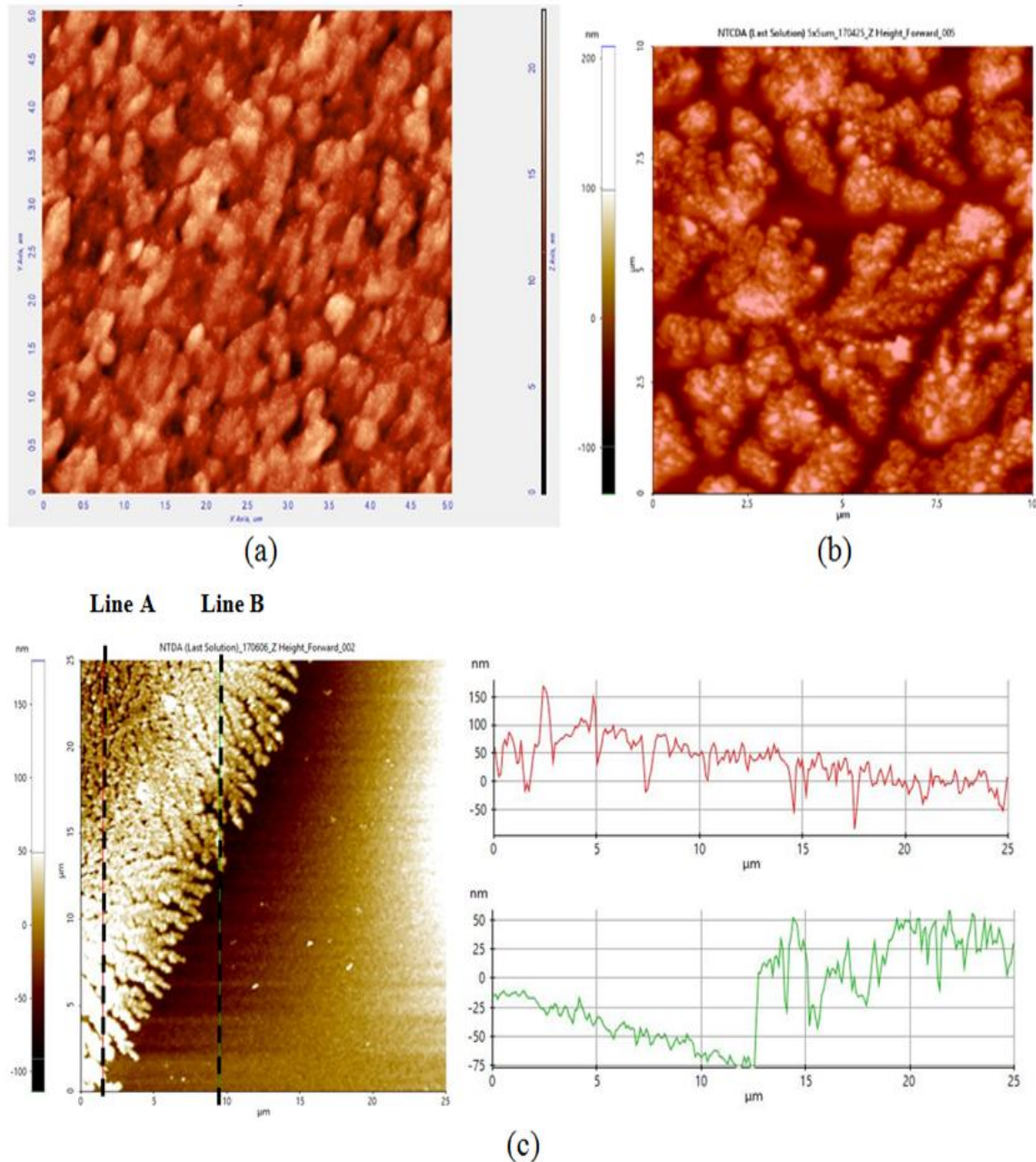


Fig. 2 (a-b) Surface images 3D of $10 \mu\text{m} \times 10 \mu\text{m}$ from atomic force microscope of bare ITO and NTCDA thin film on ITO, respectively. (c) Line profiles at edge of organic film and substrate

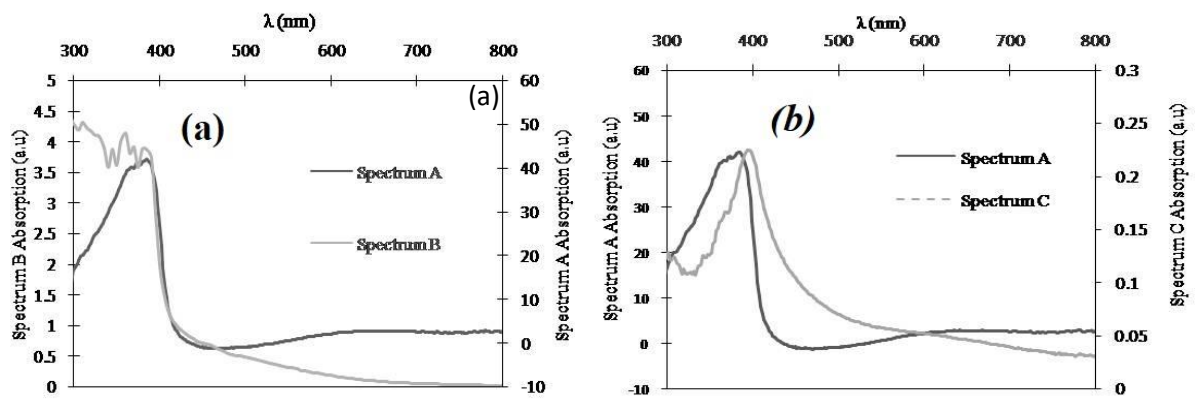


Fig. 3 Optical absorption of NTCDA solution and NTCDA films in ultraviolet and visible region

The vibrational measurement in organic samples is important to study structural change in interest material. The analysis of vibrational spectra is also useful to determine whether the solvents are still present or have completely evaporated during the drying process. First of all, smooth vibrational spectrum of polycrystalline ITO thin film was obtained to be used as reference. In the spectra of bare ITO in Fig. 4, three distinct peaks were detected at 2840 cm^{-1} , 2950 cm^{-1} and 2970 cm^{-1} . These vibrational peaks belonged to stretching C-H bond. Meanwhile, the spectrum of NTCDA film on ITO shows sharp absorption peaks that were absence in spectrum of bare ITO. One of these absorbance peaks located at $\sim 1783\text{ cm}^{-1}$ wavenumber that indicated the presence of C = O stretching due to the dianhydride carbonyl group of NTCDA structure [2]. A medium peak at $\sim 1583\text{ cm}^{-1}$ and $\sim 1300\text{ cm}^{-1}$ indicated C-O stretching vibration and C - O - C stretching NTCDA, respectively. The assignments and strength of these peaks were similar to the one in powder form indicated similarity in molecular packaging. However, there can be a weak interaction between the ITO and NTCDA as seen in the presence of several stretching modes absence in spectrum of the powder. This information most likely implied the NTCDA molecule lied flat on the substrate as seen in ref. 11. Small peaks at $\sim 3087\text{ cm}^{-1}$ were detected the in the region of C-H stretching vibration. This peak maybe related to the one observed in spectrum of bare ITO earlier. The peak shifts in this second spectra might be due to the possible migration of the electrons at the interface between ITO and NTCDA.

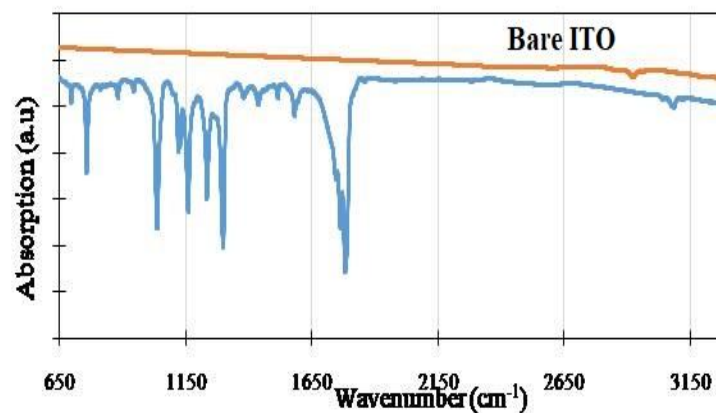


Fig. 4 FTIR spectra of ITO and ITO/NTCDA. ATR-FTIR was used to obtain the data on the vibrational mode of the films

The possibility of conformational re-arrangement occurring in HMDS-modified NTCDA film was further investigated using the vibrational spectra. Once again, comparison was made as shown in Fig. 5. Similar peaks were observed implying not much change had occurred at molecular order in the film. However, it is noted that vibrational peaks at $\sim 3087\text{ cm}^{-1}$ and 1518 cm^{-1} had disappeared when the ITO's surface was treated with HMDS. No peak shift was observed. The disappearance of the peak might be related to changing thickness of the organic layer. The range about 1500 cm^{-1} to 500 cm^{-1} is called fingerprints region where the peaks are more complicated and hard to take out the individual bonds. However, this region are important since it consists of bending vibrations of the molecule that produced pattern of the compound itself. Previous study showed that NTCDA spectrum produced unique pattern at the fingerprint region before comparing with Li and Ni metals where the spectrum is slightly changed after mixed with metal compounds [9]. So, it can be concluded from the peaks in region between 1500 cm^{-1} to 600 cm^{-1} that NTCDA molecule was not modified throughout the entire filming process.

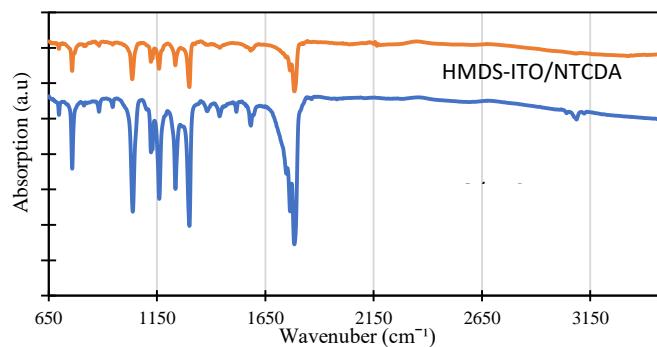


Fig. 5 Infrared absorption peaks of NTCDA films

4. SUMMARY

Thermal and chemically stable NTCDA molecule was studied as potential material in defence application. The organic semiconductor can be tuned to achieve desired electronic property. Two stacking layer films of ITO and NTCDA were fabricated using the spin coating process. Self assembled monolayers of HMDS was introduced to study the effect of surface functionalization on the interfacial electronics and optical property. The morphology of NTCDA film grown on the ITO showed high porosity and undesirable morphology to be implemented as device. The morphology can be improved with the use of HMDS at the interface. A bathochromic shift of 0.11 eV was found upon HMDS modification at interface of NTCDA film and ITO substrate indicating electronic modification on the bulk NTCDA film. From the infrared absorption spectra, it can be concluded that there is small possibility of molecular re-arrangement of the NTCDA film. There is a need of detailed measurement of XRD and FESEM to check structural conformation under this modification.

ACKNOWLEDGEMENT

The authors acknowledged the advice and technical support from Pusat Asasi Pertahanan, UPNM and Pusat Pengurusan Penyelidikan dan Instrumentasi, UKM. The work received financial support from Fundamental Research Grant Scheme: FRGS/1/2015/SG02/UPNM/03/1 and Research Acculturation Grant Scheme: RAGS/1/2015/SG0/UPNM/03/1.

REFERENCES

- [1] L. Kilian, U. Stahl, I. Kossev, M. Sokolowski, R. Fink, E. mbach, The commensurate-to-incommensurate phase transition of an organic monolayer: a high resolution LEED analysis of the superstructures of NTCDA on Ag (111), *Surface Science*, 602 (2008) 2427-2434.
- [2] E.R. Triboni, M.F.P.D. Silva, A.T. Finco, M.A. Rodrigues, G.J.F. Demets, F.H. Dyszy, M.J. Politi, Synthesis and properties of new paramagnetic hybrid bayerite from Al (0)/naphthalene dianhydride reaction, *Materials Research*, 13 (2010) 505-511.
- [3] T. Hiroto, H. Kawabata, A density functional theory study on the degradation mechanism of thin film of organic semiconductor by water molecules, *Thin Solid Films*, 516 (2008) 3287-3293.
- [4] C. Kim, M.C. Chen, Y.J. Chiang, Y.J. Guo, J. Youn, H. Huang, Y.J. Liang, Y.J. Lin, Y.W. Huang, T.S. Hu, G.H. Lee, Functionalized dithieno [2, 3-b: 3', 2'-d] thiophenes (DTTs) for organic thin-film transistors, *Organic Electronics*, 11(2010) 801-813.
- [5] R.R. Søndergaard, M. Hösel, F.C. Krebs, Roll-to-Roll fabrication of large area functional organic materials, *Journal of Polymer Science Part B: Polymer Physics*, 51((2013) 16-34.
- [6] M.D. Zidan, A.A. Mani, A.W. Allaf, Z. Ajji, A. Allahham, Optical limiting behavior of acid blue 29 under a low power CW He-Ne laser irradiation, *Acta Physica Polonica-Series A General Physics*, 115 (2009) 886.
- [7] R. Kabe, H. Nakanotani, T. Sakanoue, M. Yahiro, C. Adachi, Effect of molecular morphology on amplified spontaneous emission of bis-styrylbenzene derivatives, *Advanced Materials*, 21 (2009) 4034-4038.
- [8] M.T. Greiner, Z.H. Lu, Thin-film metal oxides in organic semiconductor devices: their electronic structures, work functions and interfaces, *NPG Asia Materials*, 5(2013) e55.[9] E. Schab-Balcerzak, A. Iwan, M. Grucela-Zajac, M. Krompiec, M. Podgorna, M.Domanski, H. Janeczek, Characterization, liquid crystalline behavior, optical and electrochemical study of new aliphatic-aromatic polyimide with naphthalene and perylene subunits. *Synthetic Metals*, 161(2011) 1660-1670.
- [10] X. Zhang, P. Bauerle, T. Aida, P. Skabara, C. Kagan, Organic electronics for a better tomorrow: innovation, accessibility, sustainability. in a white pap. from chem. sci. soc. summit San Fr. California, United States (2012).
- [11] P. Rosenow, P. Jakob, R. Tonner, Electron-vibron coupling at metal-organic interfaces from theory and experiment, *The journal of physical chemistry letters*, 7 (2016) 1422-1427.
- [13] S. Duhm, G. Heimel, I. Salzmann, H. Glowatzki, R.L. Johnson, A. Vollmer, J.P. Rabe, N. Koch, Orientation-dependent ionization energies and interface dipoles in ordered molecular assemblies, *Nature materials*, 7 (2008) 326-332.
- [14] S. Croci, A. Pecheur, J.L. Autran, A. Vedda, F. Caccavale, M. Martini, G. Spinolo, SiO₂ films deposited on silicon at low temperature by plasma-enhanced decomposition of hexamethyldisilazane: defect characterization, *Journal of Vacuum Science and Technology A: Vacuum, Surfaces, and Films*, 19 (2001) 2670-2675.