SCIENTIFIC REPORT

FINAL REPORT OF NOVEL ORGANIC MOLECULAR STRUCTURES FOR THE CONTRUCTION OF ORGANIC SOLAR CELLS AND OFETs

Guest: Cem TOZLU

Ege Univ. Solar Energy Institute,

Bornova-Izmir, TURKEY

Visit Period: 1.06.2007-28.08.2007

Host: Prof. Dr. N. Serdar SARICIFTCI

Johannes Kepler University

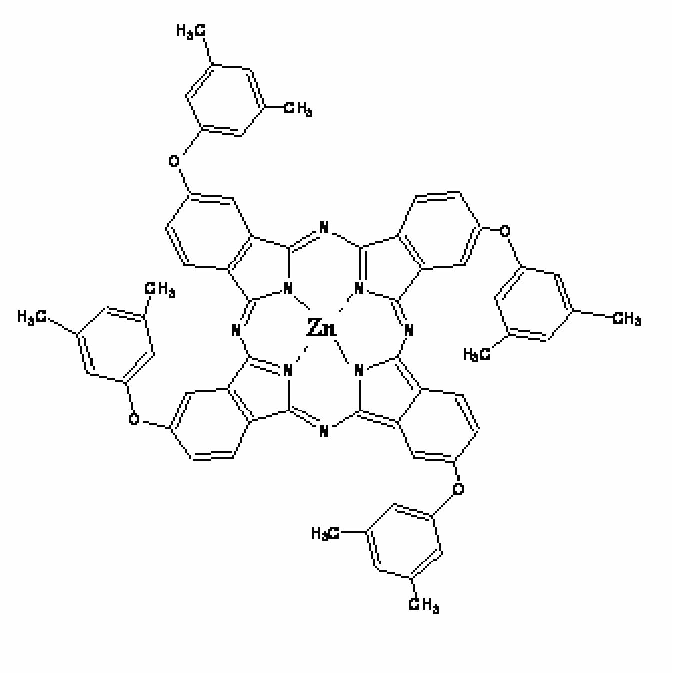
Linz Institute for Organic Solar Cells

Linz/ Austria

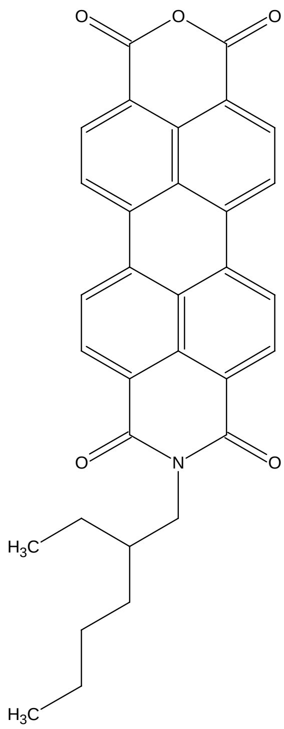
I have summarized the experimental studies at Linz Institute for Organic Solar Cell in Austruia. In the beginning of my studies, the general laboratory schooling and and safety rules was given to me for one week. I learned the construction of solar cel, transistor devices and thin film techniques in second week. I began the construction of solar cells and transistors with my materials which were synthesized in my institute after general practice.

Molecular Structures of used materials;

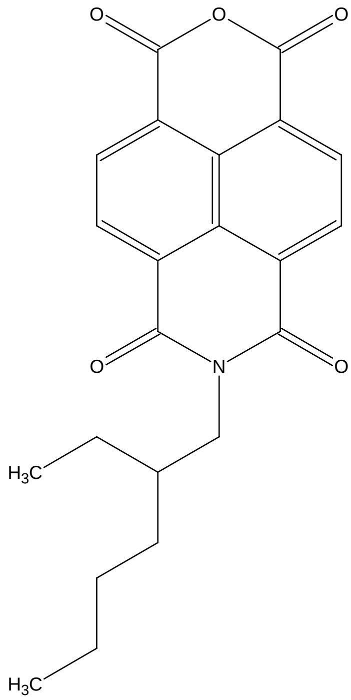
Dye sensitised solar cell and bilayer heterojunction solar cell and organic field effect transistors were fabricated by using some molecular structures; Zinc phatolacyanine, Perylene bisbenzimidazole, Naphthalene bisbenzimidazole, Ethyl hexyl Perylene monoimide, Ethyl hexyl naphthalene monoimide, N,N` -bis (2-etylhexyl)perylene dimide, N,N'-bis 2-etylhexylnaphthelene dimide. Molecular formulas of these molecules are shown below.



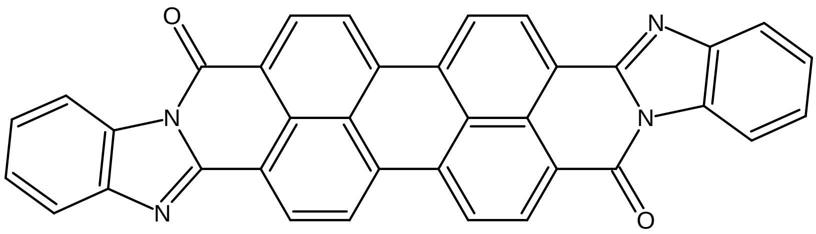
Zn(II)-2,9(10),16(17),23(24)-tetra(3,5-dimethylphenoxy)phthalocyanine



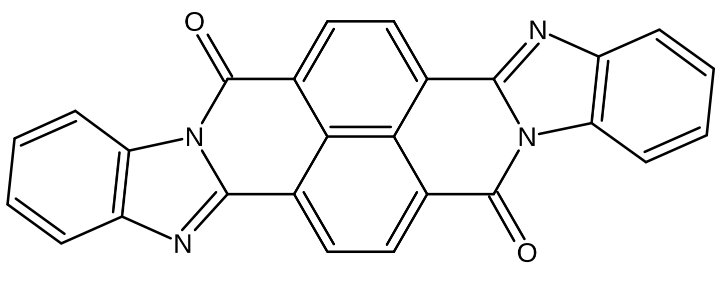
N- ethyl hexyl perylene monoimide (EHPMI)



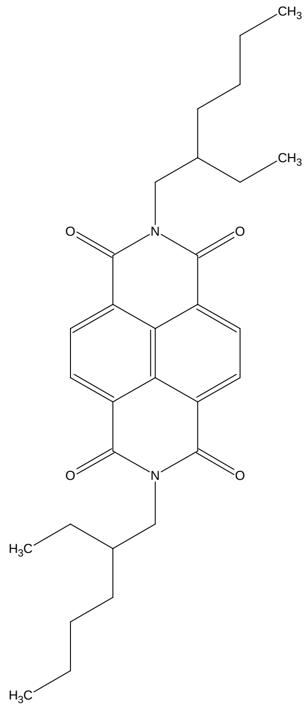
N- ethyl hexyl naphthalene monoimide (EHNMI)



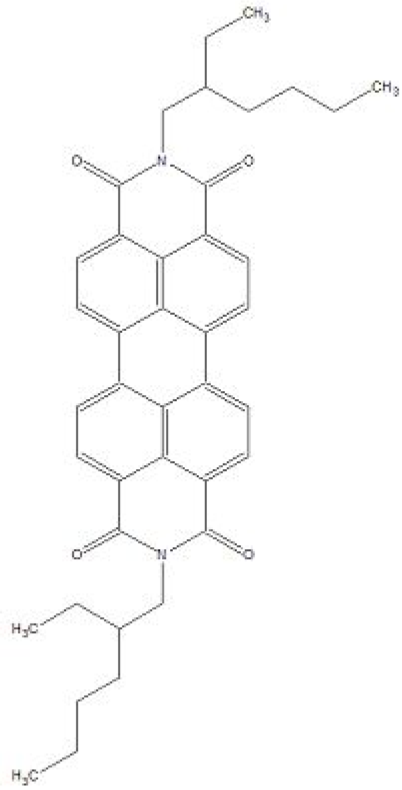
Perylene bisbenzimidazole, PBI



Naphthalene bisbenzimidazole, NBI



N,N’-di (2-etylhexyl) naphthelene diimide (EHNDI)



N,N` -di (2-etylhexyl) perylene diimide (EHPDI)

As first step, I started to my studies by making bulk heterojunction solar cell by using Zn-dimethylphenoxy phthalocyanine as a p type material. PEDOT:PSS (poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) was spincoated on transparent ITO (indium tin oxide) glass firstly. The blend of PCBM:ZnPc was prepared at 2:1 weight concentration ratio and spin coated on PEDOT:PSS:ITO thin film. 0.6nm of LiF and 100nm of Al are thermally evaporated under high vacuum for metal contact. The structure of solar cell is shown Figure1. The absorption spectrum of Zn-dimethylphenoxy phthalocyanine in chloroform is given Figure2.

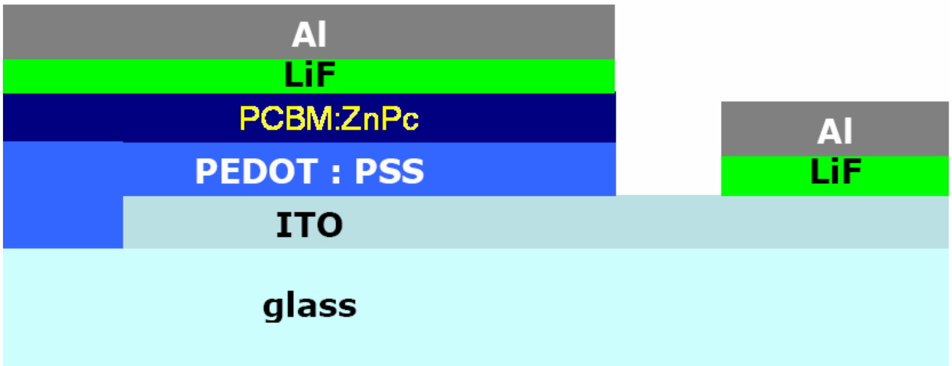


Figure1. Solar cell structure

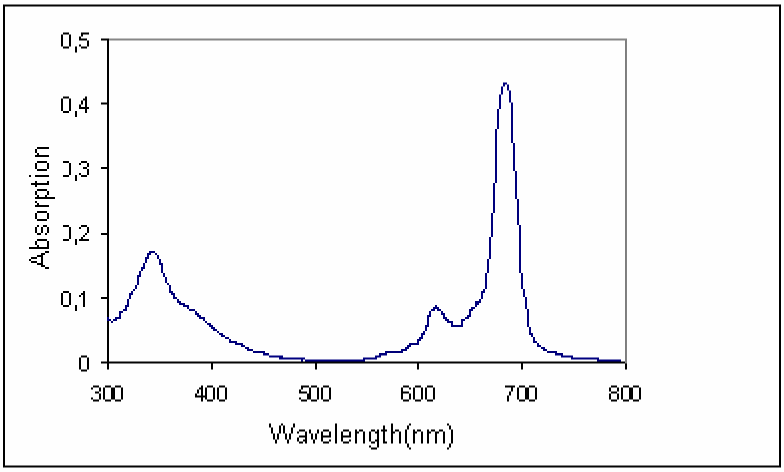
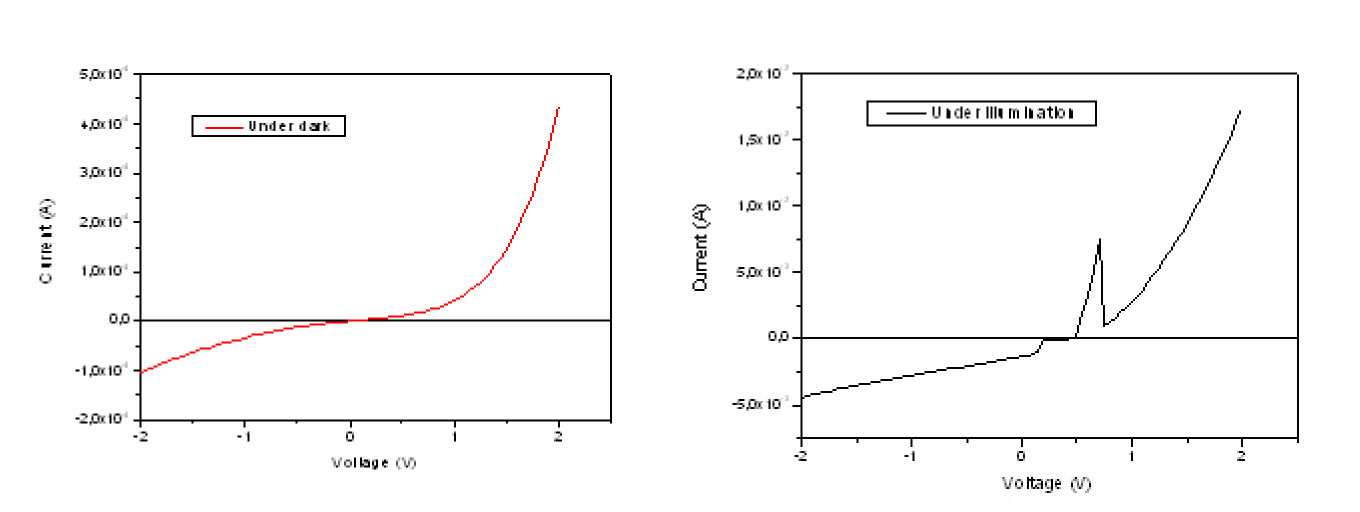


Figure2. The absorption spectrum of Zn-dimethylphenoxy phthalocyanine

Two absorption peaks where are at 620nm, 684 nm wavelengths are obtained in the visible region for ZnPc in chloroform. The I-V curve of PCBM:ZnPc solar cell is given Figure 3.



a b

Figure3. I-V curves of PCBM:ZnPc bulk heterojunction solar cell under dark and illumination conditions

The short circuit current of PCBM:ZnPc bulk heterojunction solar cell is 1.3 mA/cm^2 and open circuit voltage 450mV under 100mW/cm^2. Maximum current and voltage of PCBM:ZnPc are 0.73mA/cm^2 and 300mV respectively. The efficiency and fill factor values of solar cell are 0.22% and 0.39 respectively. The incident photon to current efficiency (IPCE) versus wavelength is shown in Figure4. Maximum IPCE value was 7.5% at 630 nm.

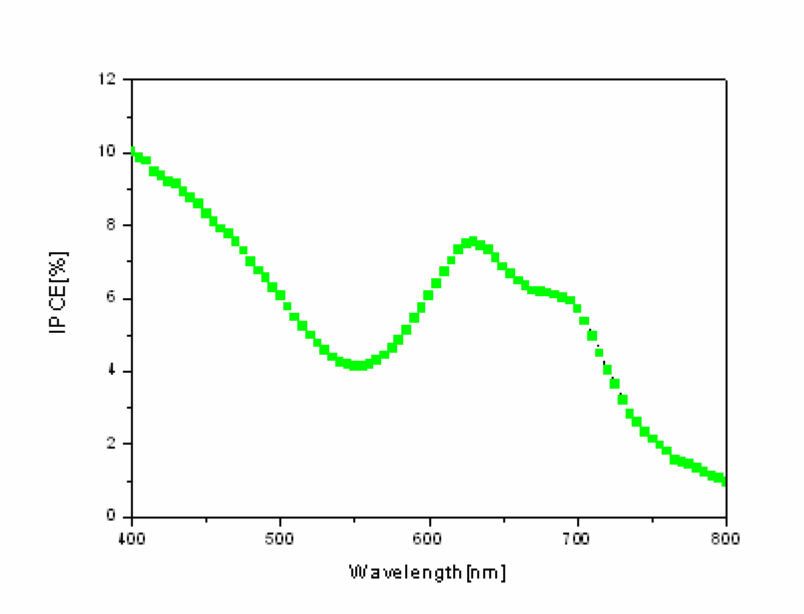


Figure4. IPCE curve versus wavelength

The amount of ZnPc derivative was not enough to optimize the solar cell performance and other experimental processes. I ordered the new synthesing material for same derivative. the solubility of this material was not well as former derivative when I tried the new ZnPc derivative was came form my insititute and The film on PEDOT:PSS has very high porosity.

In the second step of my studies, I used some of organic materials in the application of solution processed organic field effect transistor. Bottom gate structure was used for all organic field effect transistors on this study as shown Figure 5. 0.6nm of LiF and 60nm of Al were thermally evaporated under high vacuum ($\approx 10^{-4}$ mbar) for top source and drain contacts through a shadow mask. The channel length, *L*, of all devices was 47 µm and the channel width, *W*, was 2 mm.

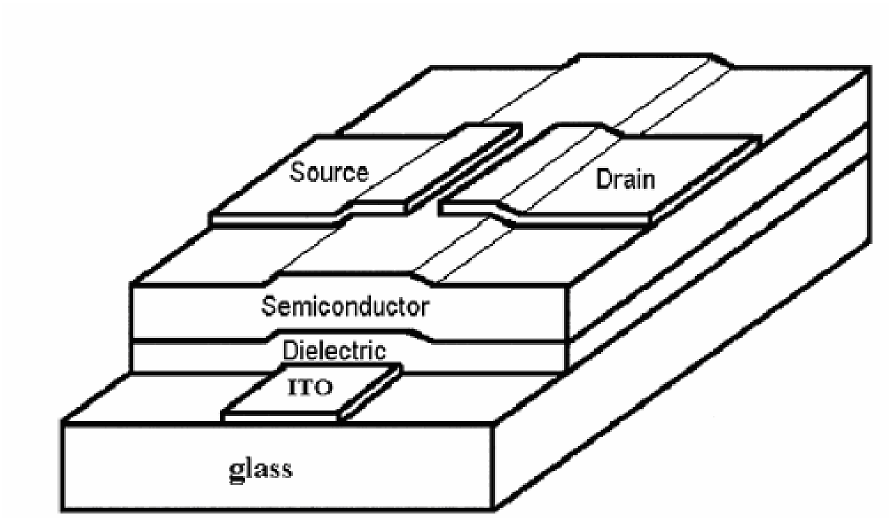


Figure5. The structure of organic field effect transistor

I chose poly-4-vinylphenol (PVP) and polyvinyl alcohol (PVA) polymer as dielectric materials and I prepared these dielectric solutions in isopropanol and water respectively. The thin film of dielectric materials was formed by spin-cast in 7% wt ratio at 1500 rpm. N-buthyl 1,8- Naphthalene monoimide (BNMI), N-ethyl hexyl-1,8- Naphthalene monoimide (EHNMI) and ethyl hexyl-1,8- perylene monoimide (EHPMI) were used the active semiconductor materials and thin film layers of these semiconductors were formed by spin-cast from 1% wt ratio in chloroform and acetonitrile solvents. The output and transfer characteristics of these materials are shown in Figure6,7,8,9.

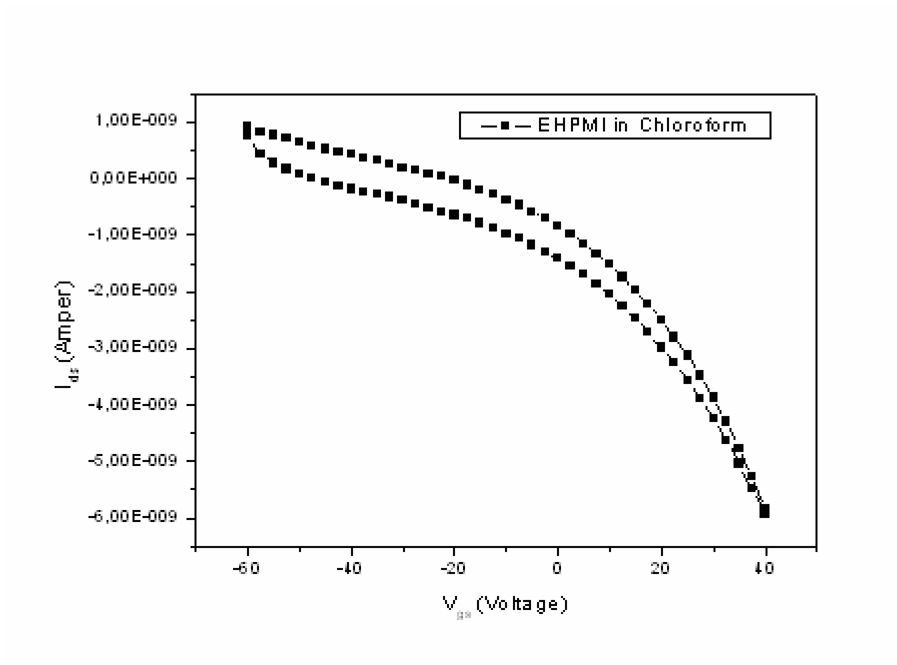


Figure6. The transfer characteristics of EHNMI, V_{ds}: 40V

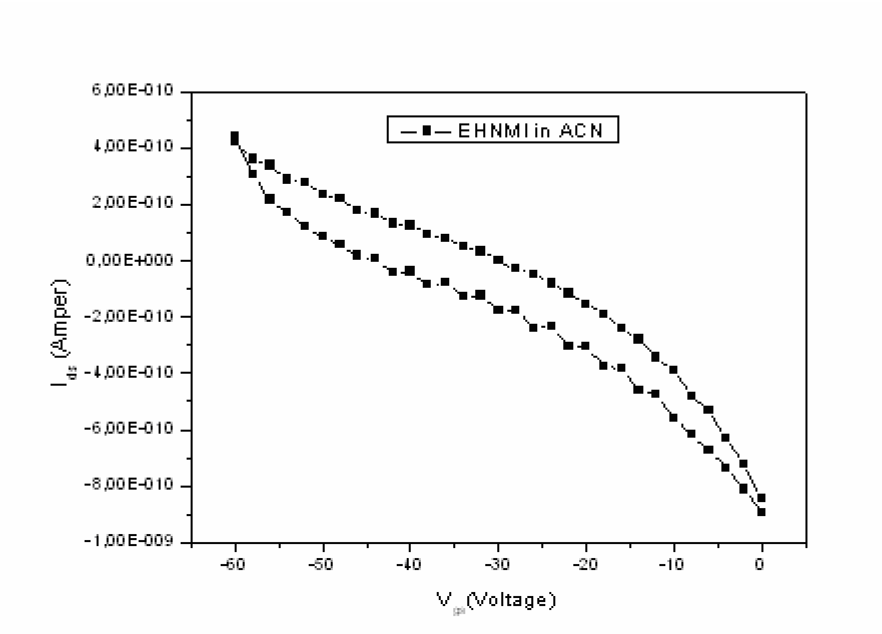


Figure7. The transfer characteristics of EHNMI, V_{ds}: 40V

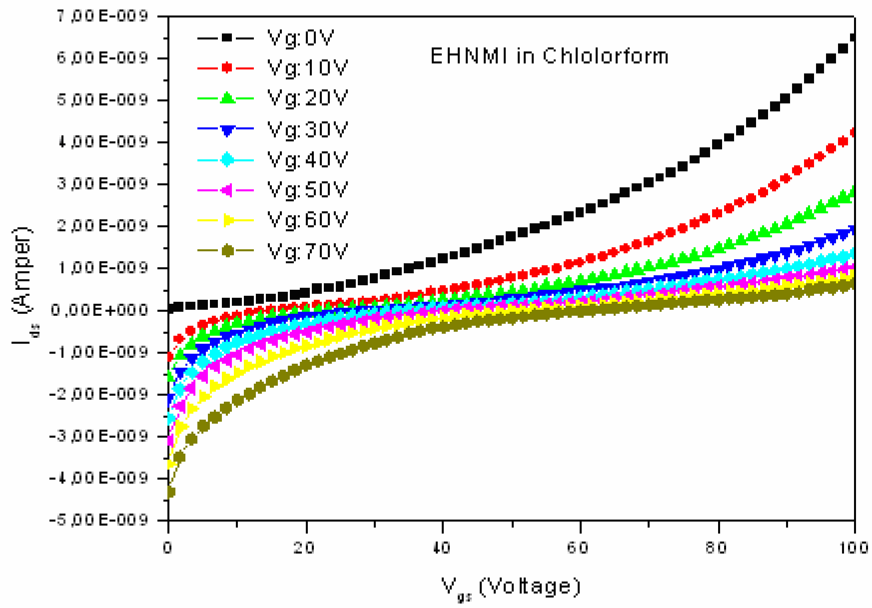


Figure8. The output characteristics of EHNMI for n-type transistor

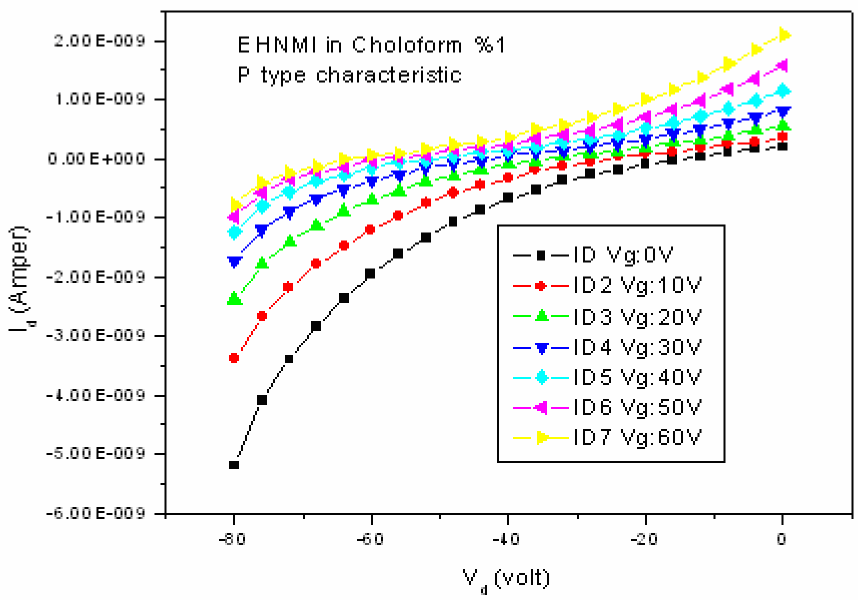


Figure9. The output characteristics of EHNMI for p-type transistor

The ethyl hexyl monoimide derivatives of perylene and naphthalene didn't exhibit any transistor characteristics as shown in Figure 6,7,8,9. I can say that any accumulation mode of electron and hole don't form between dielectric and semiconductor interface in the case of using perylene and naphthalene monoimide derivatives.

I used ethyl hexyl perylene diimide (EHPDI) and ethyl hexyl naphthalene dimide (EHNDI) derivatives as active semiconductor for transistors after experiments on monoimide derivatives of them. I applied spin-cast and vacum evaporation methods for thin film forming on PVA, PVP and divinyltetra-methyldisiloxanebis(benzocyclobutene) (BCB) dielectric films. Thin films of active layers were formed by spin-cast methods at 1500 rpm in 1% wt ratio for each of them. Chloroform and Chlorobenzenol were used to dissolve EHPDI, EHNDI respectively. The transfer and output characteristics of each organic semiconductor are shown following figures.

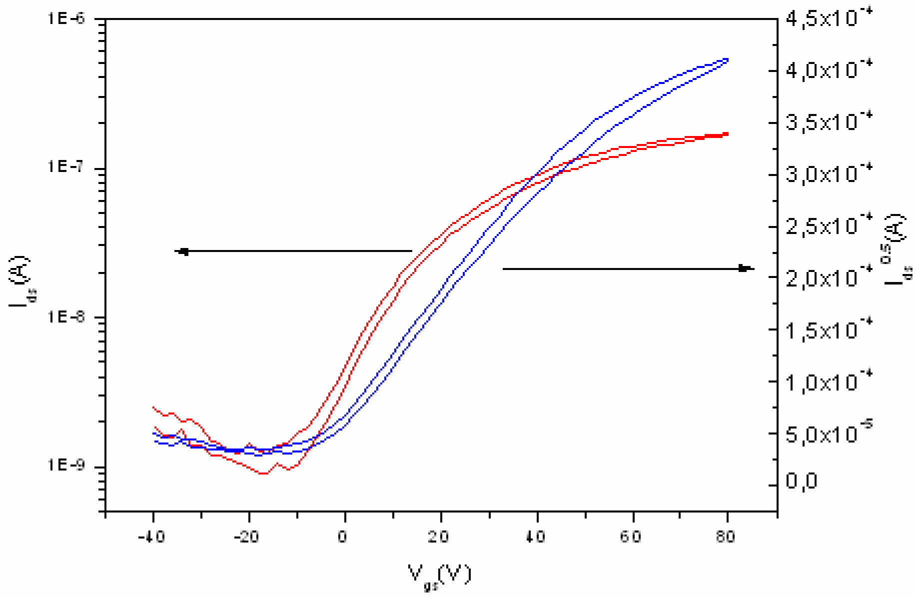


Figure10. The transfer characteristic of EHPDI on PVP dielectric, V_{ds}: 40V

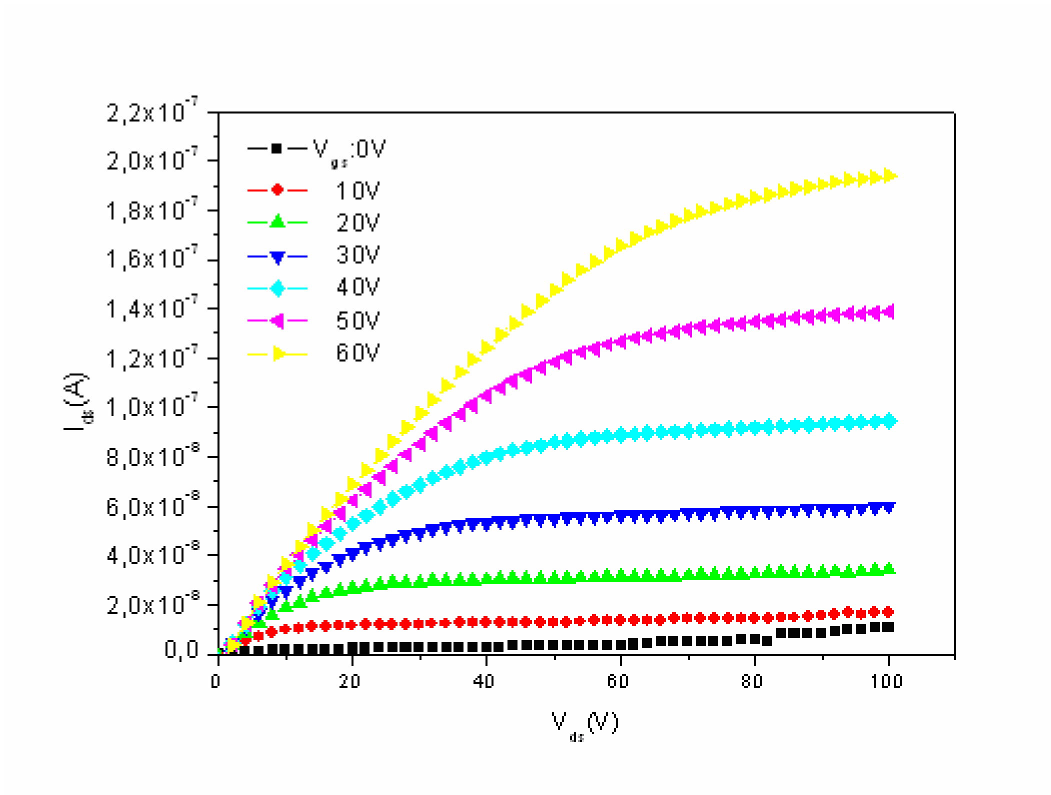


Figure11. The output characteristic of EHPDI on PVP dielectric

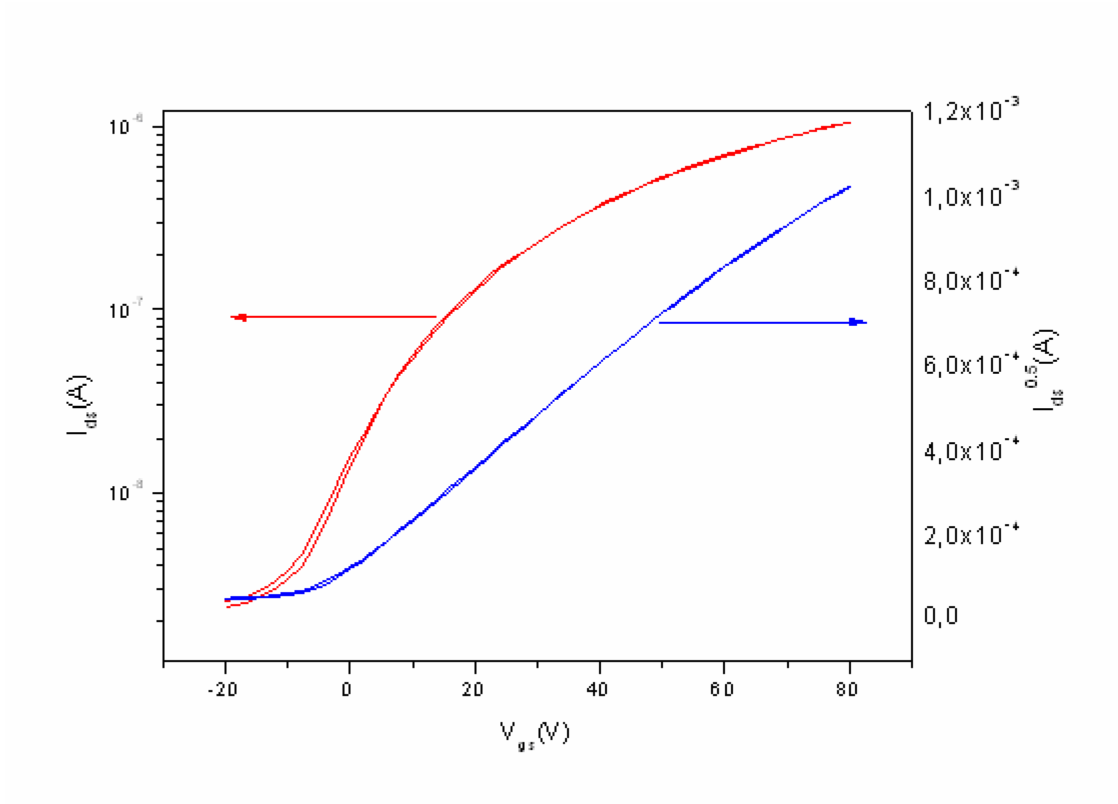


Figure12. The transfer characteristic of EHPDI on BCB dielectric, V_{ds}: 40V

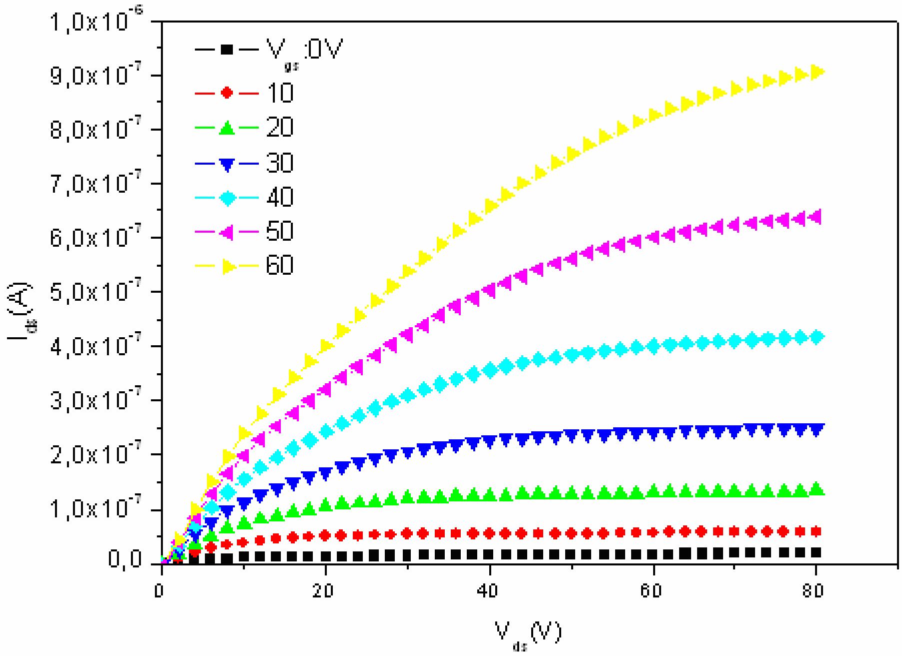


Figure13. The output characteristic of EHPDI on BCB dielectric

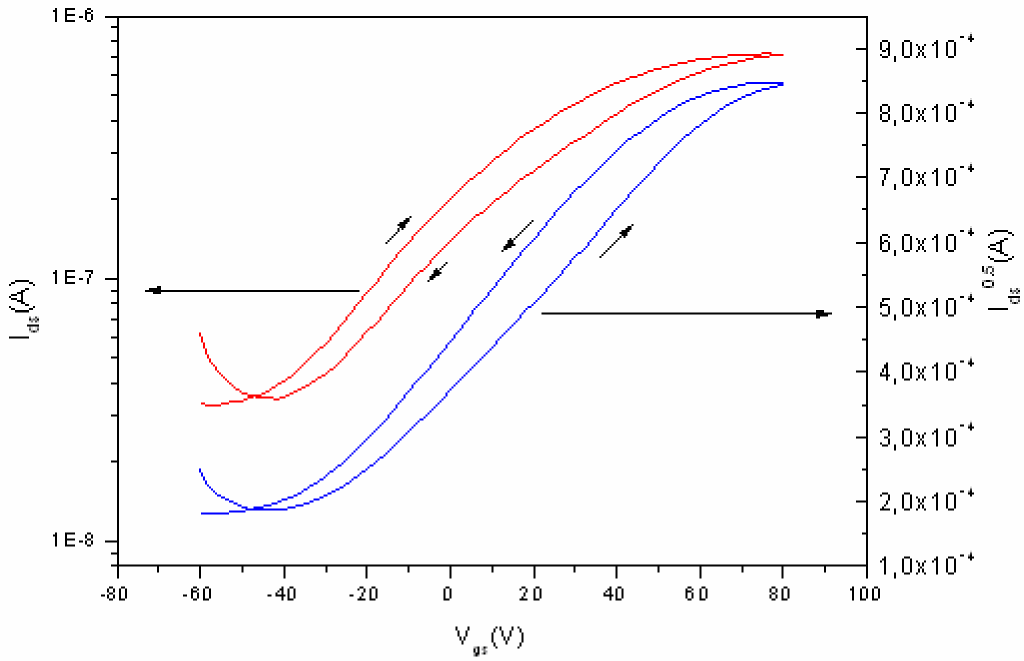


Figure14. The transfer characteristic of EHPDI on PVA dielectric, V_{ds}: 40V

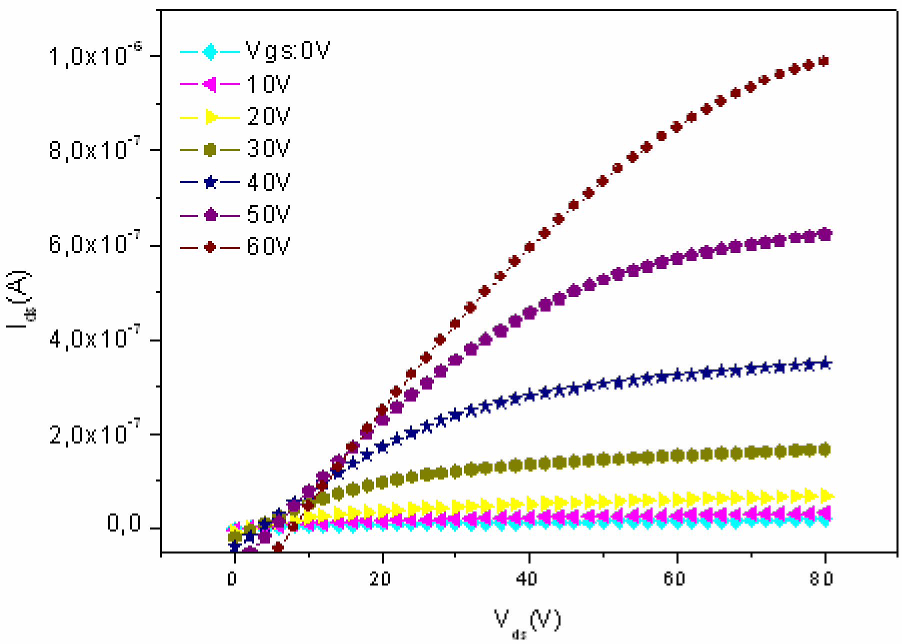


Figure15. The transfer characteristic of EHPDI on PVA dielectric

Solution-processed n-type organic transistor has been fabricated by using ethyl hexyl perylene diimide derivative as seen above figures. The transfer curves were obtained at V_{ds}:40V. I calculated the mobility from standard transistor equations (1) and the best electron mobility, μ_e , with an order of 10^{-3} was obtained by using BCB dielectric. For PVA and PVP dielectric, the mobility of EHPDI is an order of 10^{-4}. on/off ratio of device is about 10^3 and the value of threshold voltage is -5V as seen in Figure12. In addition to this experiment, the small hysteresis is observed on PVA dielectric as shown Figure 14.

$$\mu = \frac{2\,L}{WC}\left(\frac{\partial\sqrt{I_{ds}}}{\partial V_{gs}}\right)^2 \qquad (1)$$

Naphthalene bis-benzimidazole (NBI) and perylene bis-benzimidazole (PBI) were used as an active semiconductor for transistor separately. Naphthalene bis-benzimidazole is used as n-type semiconductor in bilayer heterojunction solar cell in literature. These molecules are not soluble any solvents. Thus 60nm and 100nm of NBI were evaporated under vacuum ($\approx 10^{-5}$ mbar) at rate of 0.04nm/sec. BCB and PVA were used as dielectric materials and semiconductors were evaporated on these dielectrics. The transfer and output characteristics of NBI are shown following figures.

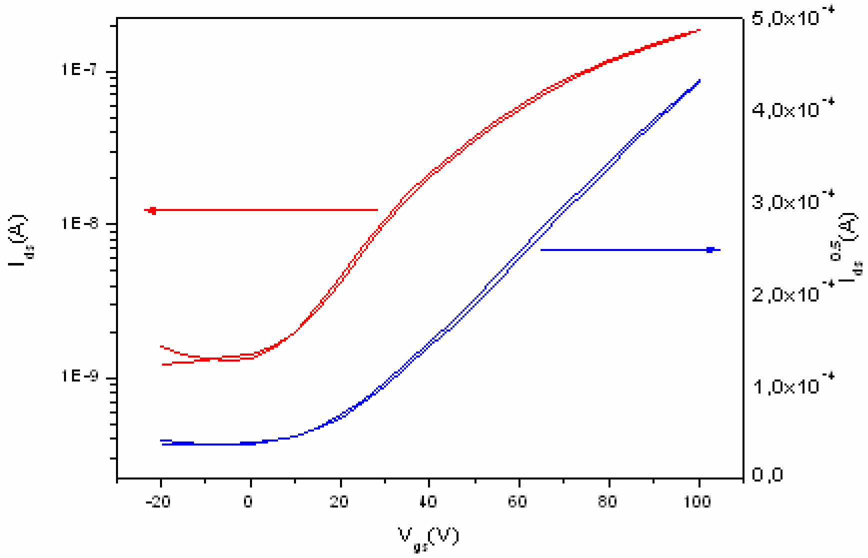


Figure17. The transfer characteristic of 60nm of NBI on BCB dielectric.V_{ds}:40 V

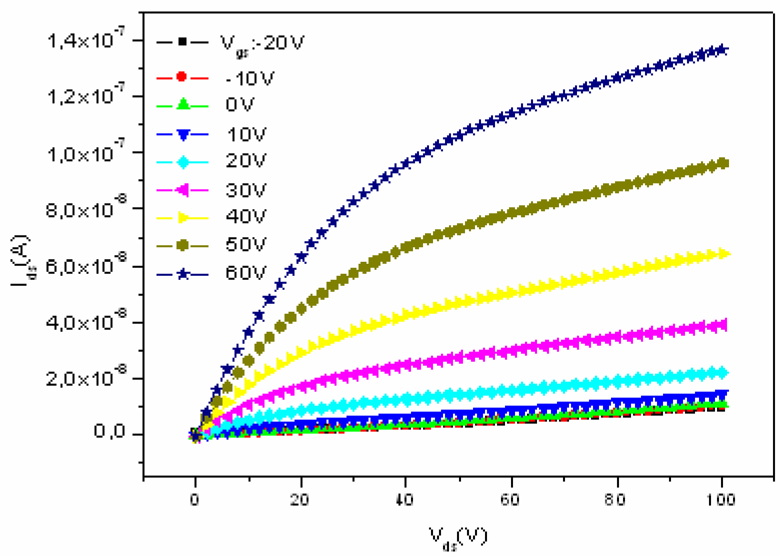


Figure16. Output characteristic of NBI on BCB dielectric. The thickness of NBI is 60nm

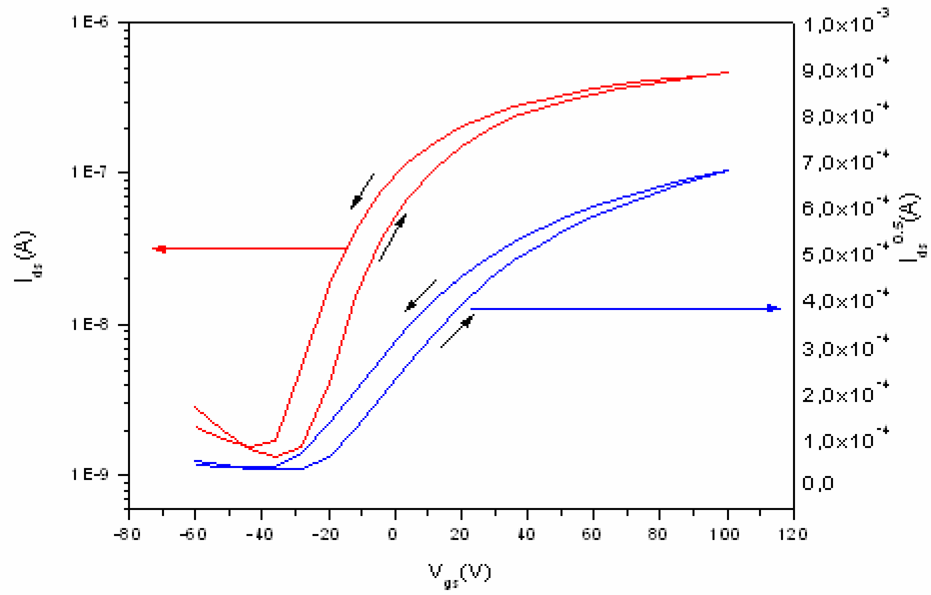


Figure18. The transfer characteristic of NBI on PVA dielectric. The thickness of NBI is 100nm, V_{ds}: 40V

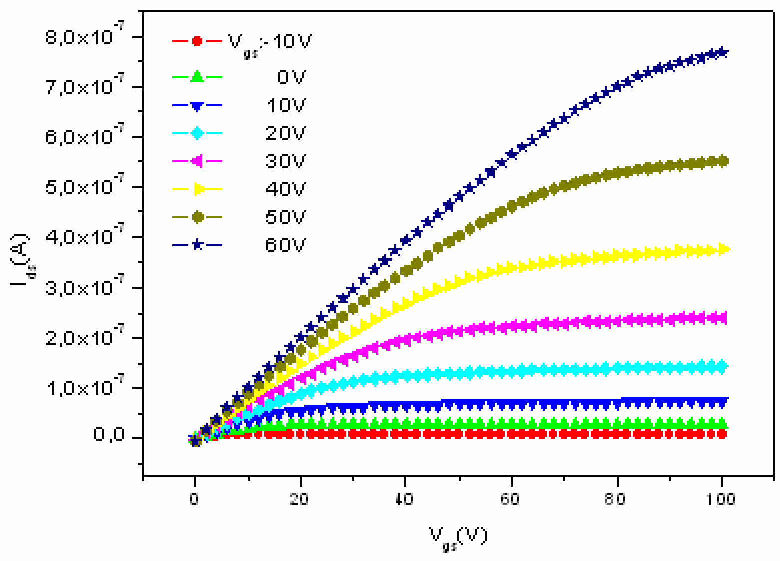


Figure19.The output characteristic of 100nm of NBI on PVA dielectric.

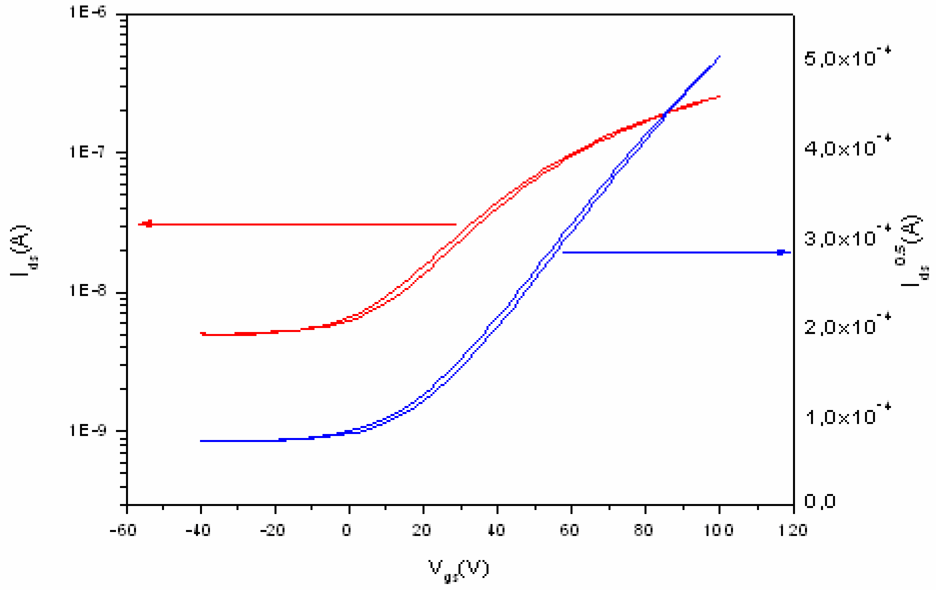


Figure20.The transfer characteristic of NBI on BCB dielectric. The thickness of NBI is 100nm, V_{ds}: 40V

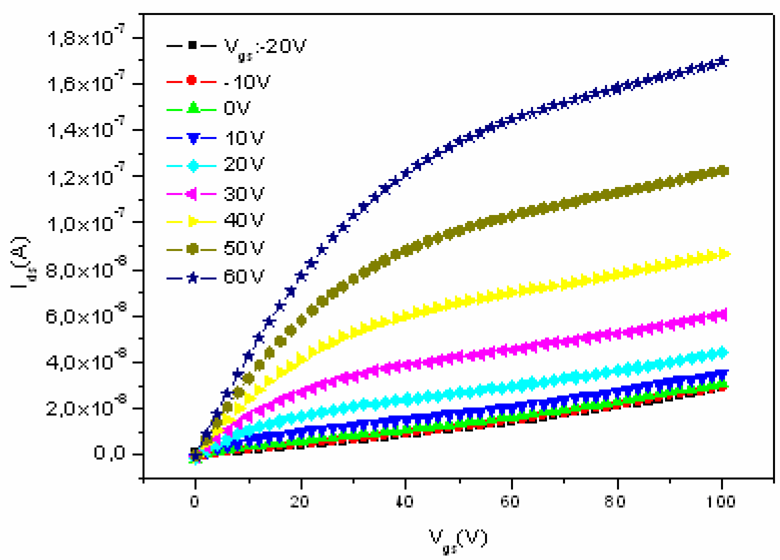


Figure21.The output characteristic of 100nm of NBI on BCB dielectric.

N-type transistor characteristic was observed for NBI semiconductor. NBI shows good output characteristics on PVA dielectric compared with BCB dielectric. Its electron mobility, μ_e, is an order of 10^{-3} and on/off ratio is about 10^2. the electron mobility of device for BCB dielectric is an order of 10^{-4}. I investigated metal contact effects on NBI transistor. I evaporated only 60nm of Al for source and drain contact and 100nm of NBI on PVA dielectric. Figure 22 and 23 shows the transfer and output characteristics of NBI transistor with only Al contact.

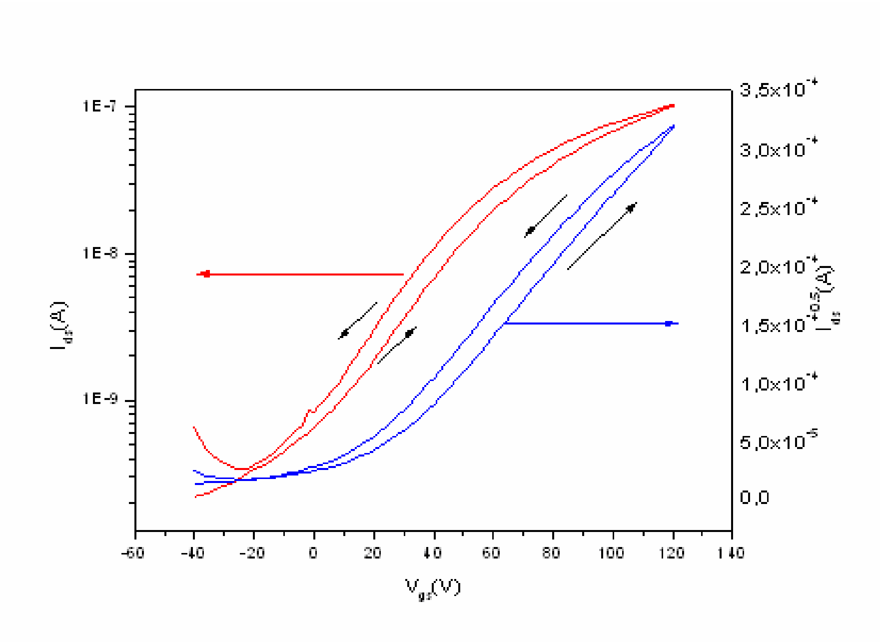


Figure22. The transfer characteristic of NBI on PVA with Al contact, V_{ds}:40V

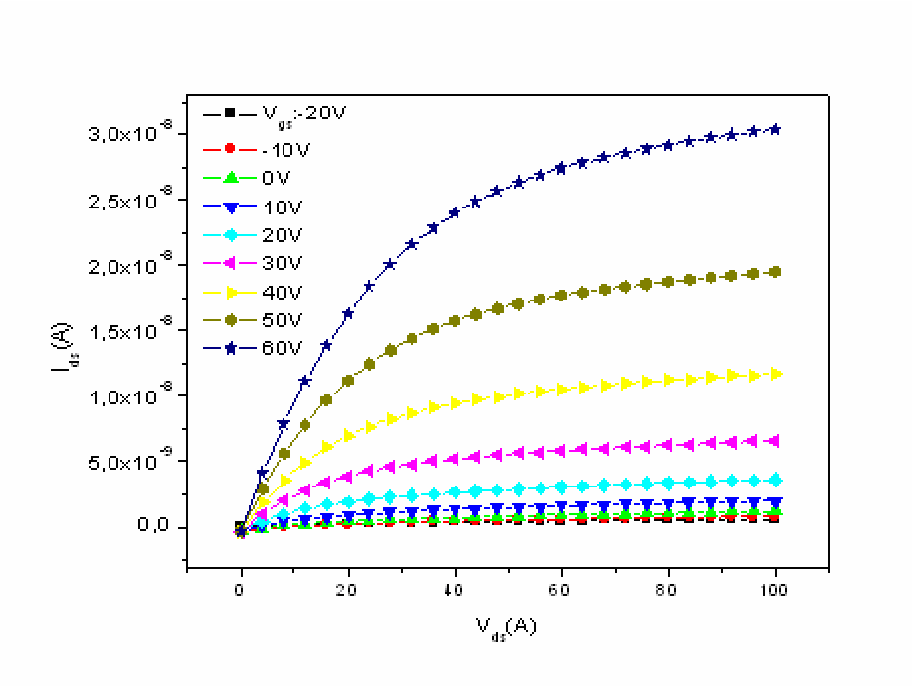


Figure23. The output characteristic of NBI on PVA with Al contact

For Al contact, The saturated drain-source current is lower than LiF:Al contact as shown Fig 22 and 18) but it exhibits good transistor characteristic as shown Figure23. The electron mobility was calculated as an order 10^{-5} for NBI transistor with Al contact. LiF provides higher electron mobility compared with only Al metal contact. LiF provides electron injection from contact to semiconductor as result of higher mobility.

The other bis-benzimidazole derivative which is perylene bis-benzimidazole (PBI) was used active semiconductor for transistor. As top source and drain contacts, only Al was evaporated under high vacuum ($\approx 10^{-4}$ mbar). 60 nm of PBI was evaporated under vacuum ($\approx 10^{-5}$ mbar) at rate of 0.04nm/sec. The transfer and output characteristics of PBI are shown in Figure24 and 25. N-type transistor characteristic was observed for PBI semiconductor as seen Figure 24 and 25. The electron mobility of this device is an order of 10^{-4} and on/off ratio is about 10^2.

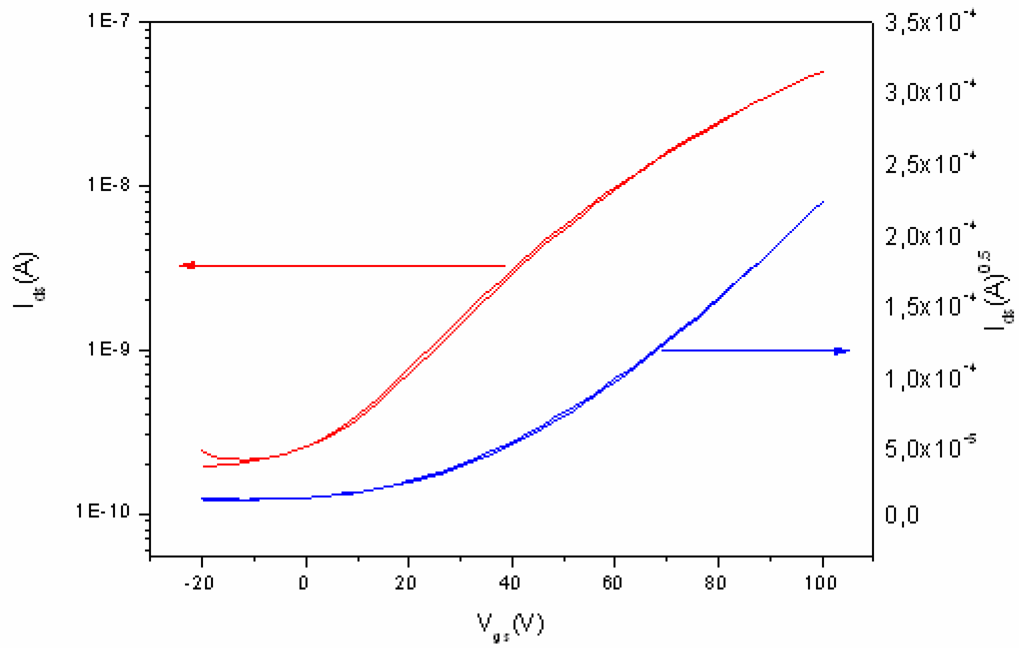


Figure24. The transfer characteristic of PBI, V_{ds}: 40V

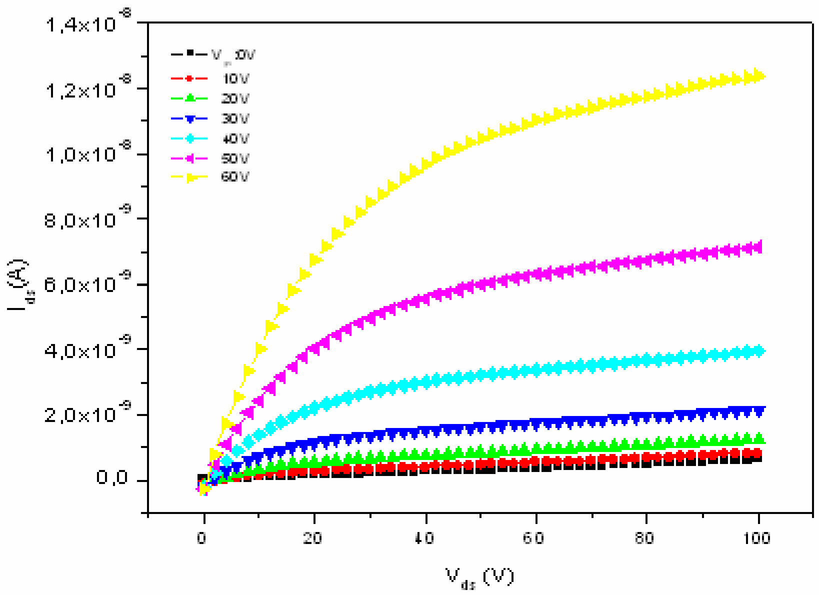


Figure25. The output characteristic of PBI

Ethyl hexyl perylene diimide (EHPDI) and ethyl hexyl naphthalene diimide (EHNDI) were used as the last semiconductors. In the beginning of my studies I fabricated solution-processed n-type transistor by using EHPDI semiconductor. In this step, EHPDI was evaporated under high vacuum in order to compare with solution process. 60nm of EHPDI was evaporated on BCB dielectric under high vacuum ($\approx 10^{-5}$ mbar) at rate of 0.1nm/sec. LiF/Al (0.6/60nm) was evaporated as top source and drain contact thorough shadow mask. The electron mobility of EHPDI transistor is an order of 10^{-3} and on/off ratio is about 10^{2}. The transfer and output characteristics of EHPDI are shown in Figure26 and 27.

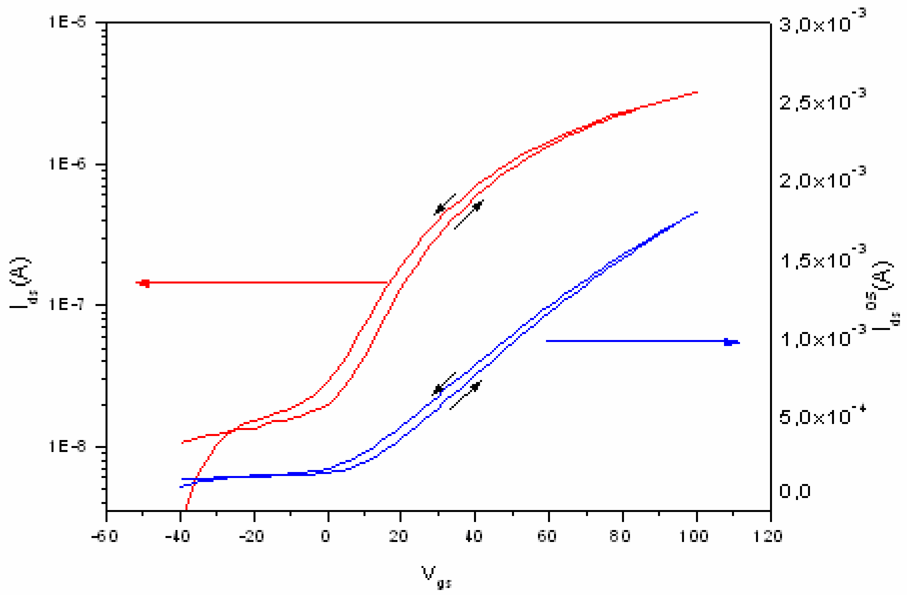


Figure26.The transfer characteristic of PDI

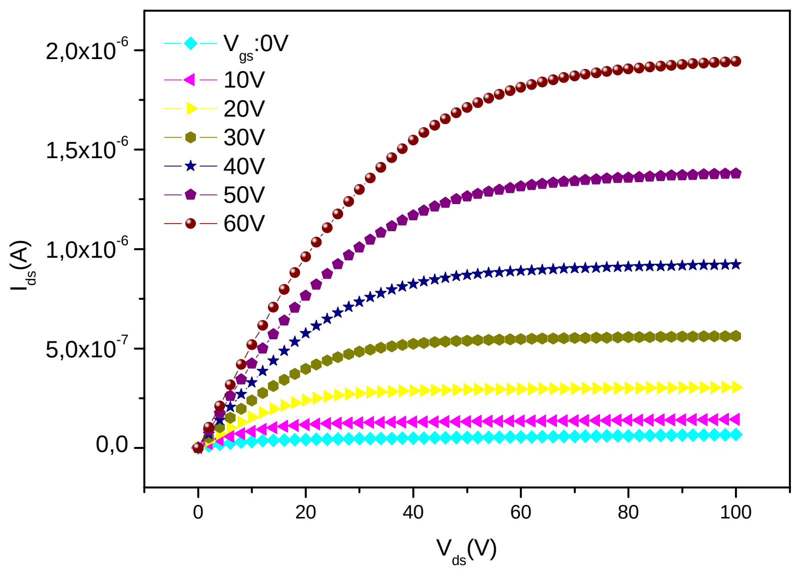


Figure27. The output characteristic of PDI

At last step of my studies, Ethyl hexyl Naphtalene diimide (EHNDI) was evaporated under high vacuum on PVA dielectric. The thickness of EHNDI is 120nm and LiF/Al (0.6/60nm) was evaporated as top source and drain contact. The transfer output characteristics of EHNDI are shown in Figure28and 29. The mobility of EHNDI is order of 10^{-2} $cm^2/V.s$ and on /off ratio is about 10^5

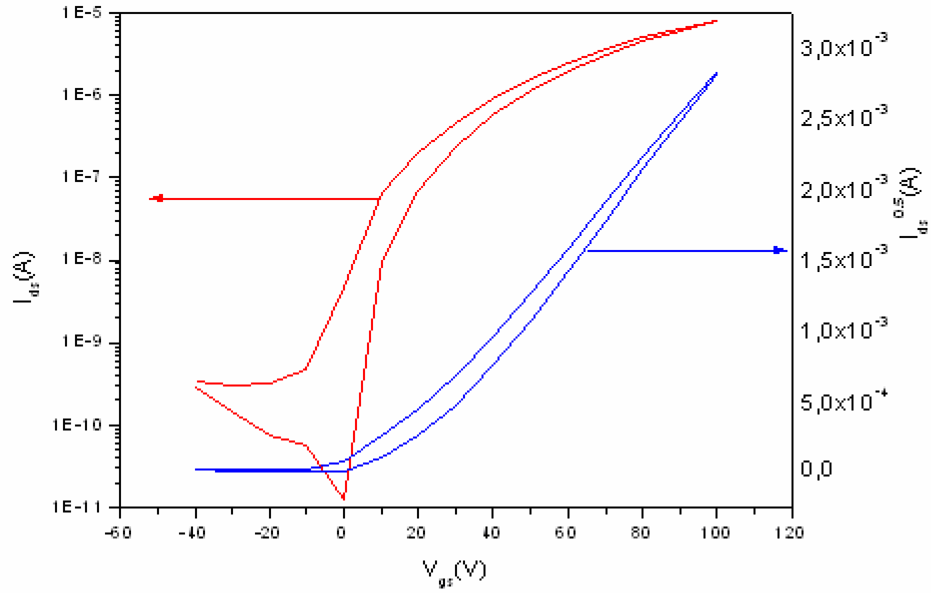


Figure28. The transfer characteristic of EHNDI on PVA

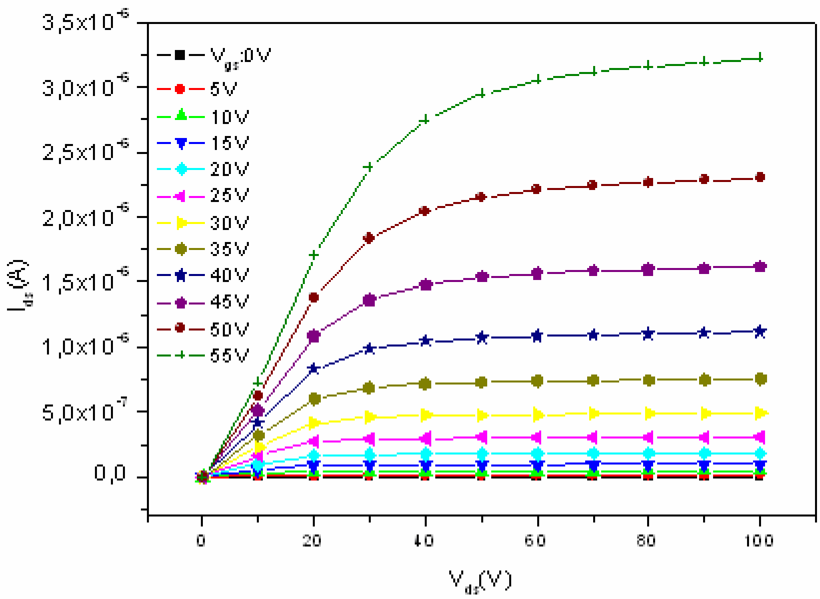


Figure29. The transfer characteristic of EHNDI on PVA

SUMMARY

In my first work plan, I demonstrated solution-processed bulk heterojunction ZnPc solar cell with PCBM. But we must purify ZnPc in order to obtain high efficiency and good film structure. If we fabricate this soluble ZnPc solar cell, we will start new concept solar cell fabrication.

In my second work plan, I fabricated solution-processed and evaporation-processed transistors. All transistors show n-type transistor characteristic. These devices can be useful in electronic circuit for electron transport. I obtained highest efficiency by using ethyl hexyl naphthalene diimide derivative with an order of 10^{-2}. Naphtalene derivatives show good transistor characteristics on PVA dielectric. Perylene derivatives show good transistor characteristic on BCB dielectric as seen figures. Organic dielectric affects semiconductor/dielectric interface. Thus, organic dielectric play important role on transfer characteristics of devices.

Cem TOZLU

Ege University Solar Energy Institute

Izmir/TURKEY