



ISSN: 0976-3376

Available Online at <http://www.journalajst.com>

ASIAN JOURNAL OF  
SCIENCE AND TECHNOLOGY

Asian Journal of Science and Technology  
Vol. 08, Issue, 05, pp.4729-4735, May, 2017

## RESEARCH ARTICLE

### DESIGN STUDY AND CHARACTERIZATION OF HIGHLY EFFICIENT ORGANIC SOLAR CELLS WITH NOVEL SOLUBLE DONOR MATERIALS USING INKJET PRINTING TECHNIQUE

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#### ARTICLE INFO

##### Article History:

Received 14<sup>th</sup> February, 2017  
Received in revised form  
21<sup>st</sup> March, 2017  
Accepted 09<sup>th</sup> April, 2017  
Published online 17<sup>th</sup> May, 2017

##### Key words:

Photovoltaic (PV)  
Poly 3-hexylthiophene (P3HT)  
phenyl-C61-butyric acid methyl.

#### ABSTRACT

The main objective of this project is to develop organic solar cells with highly soluble novel donor materials using inkjet printing technique. It can produce cheap and efficient photovoltaic (PV) and organic solar cells (OSC) thought as the devices which will be used in future for these purposes. The organic solar cells mostly is composed of a light absorbing poly 3-hexylthiophene (P3HT) donor polymer and a soluble C60 bulky ball derivative, typically phenyl-C61-butyric acid methyl ester (PCBM), acting as an acceptor. (this stage will cost . The main focus in this field is to increase the power conversion efficiency. Since it has not yet been possible to replace the C60 derivatives with equally efficient electron acceptors, the preferred way to improve solar cell efficiency is through choice of new type of materials having donor properties The usage of inkjet method which is very cheap and whose application is very simple in the production of these PV and OSC cells will be very effective in the reduction of the energy costs. It is foreseen that application of organic solar cells by using this inkjet technique is an easier, faster, low cost, and established technology. It allows printing on flexible substrates in ambient conditions with digital patterning options in mass production up to 150 m<sup>2</sup>/h.

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## INTRODUCTION

The bulk hetero junction solar cell is one of the most promising applications for organic solar cells bringing together chemistry, physics and material engineering. The combination of these diverse areas of research promises to yield advances in renewable energy through the creation of promising, environmental and alternative tool. Devices based on nano size have emerged an alternative for world energy consumption and very friendly for environmental platforms. Various materials based on various aspects have been developed that improve harvesting of solar spectra and efficiency. To achieve high efficiencies and absorption on broader spectra, new type of organic materials having low band gap and good solubility, presenting desired morphology are necessary to synthesize and apply on organic solar cell field. Regarding this, these kinds of materials have been widely investigated because of the high efficiencies, easier synthesis, purification and application. To date, application in organic solar cell based on various techniques and inkjet printing is promising, faster and new that already have demonstrated in many papers. In order to utilize new organic materials, solubility is essential property for synthesis and inkjet printing, as well.

Several types of organic materials have been developed including polymers, small molecules having either donor or acceptor properties, or both of them. Among these organic materials small molecules have attracted great attention due to long term stability, easy synthesis procedures and high solubility. Furthermore, many types of organic materials have been developed by arranging morphology. However, in application step, while blending donor and acceptor many undesired cases happened. In this stage, a new aspect is needed. In this regard, organic small molecules such as soluble triarylamine derivatives are very promising candidate materials because of tuneable structure and providing high donor properties.

### Project Objectives

#### Organic Donor and Acceptor Molecules

A widely employed approach consists in synthesizing hybrid conjugated polymers containing alternate donor and acceptor building blocks. In spite of the important progress accomplished in the optimization of the performances of polymer-based bulk hetero-junctions cells (BHJ), polymeric donor still pose some specific problems related to the control of their structural regularity, molecular weight and reproducibility. Recently, a possible solution to these problems

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has been proposed that consists of replacing conjugated polymers by soluble small molecules as a donor material in BHJ solar cells. In addition to specific advantages in terms of structural definition, reproducibility and purification, molecular donors allow more straightforward and reliable analyses of the relationships between chemical structure and electronic properties than polydisperse polymers (Evaluation of bis-dicyanovinyl short-chain conjugated systems as donor materials for organic solar cells, *Solar Energy Materials & Solar Cells* 95 (2011) 462–468).

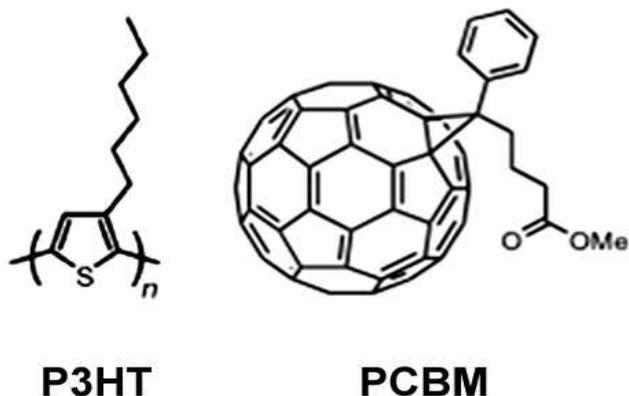


Figure 1. Structure of PCBM and P3HT

#### Donor materials

are used for to donate electron to system and acceptor materials to keep electrons. Donor materials are generally used amines, carbazoles, to date best known material is alkoxy derivative triarylamine and acceptor materials are generally have cyanic, halogene or oxygen groups, but best known materials is PCBM which is quite different from common molecules (Figure 1.). Our main purpose is to synthesize, characterize and apply new type of highly soluble and efficient materials on device with inkjet technique.

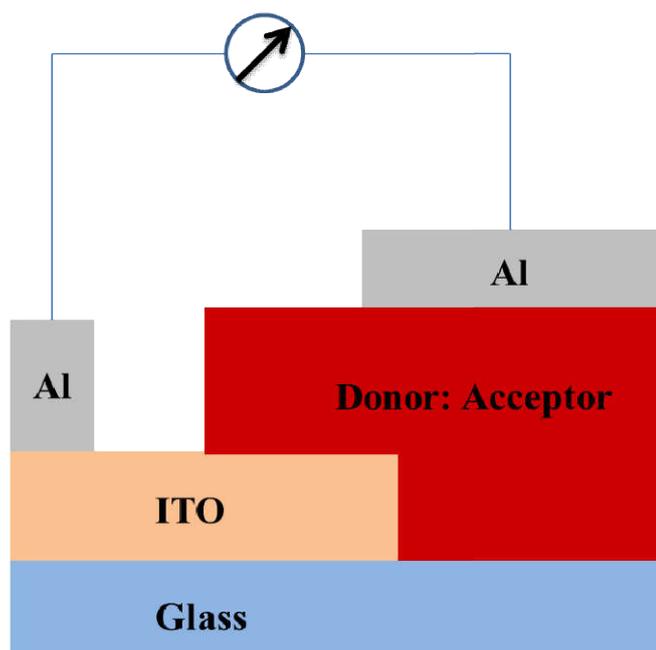


Figure 2. Schematic of the basic structure of a bulk heterojunction organic solar cell

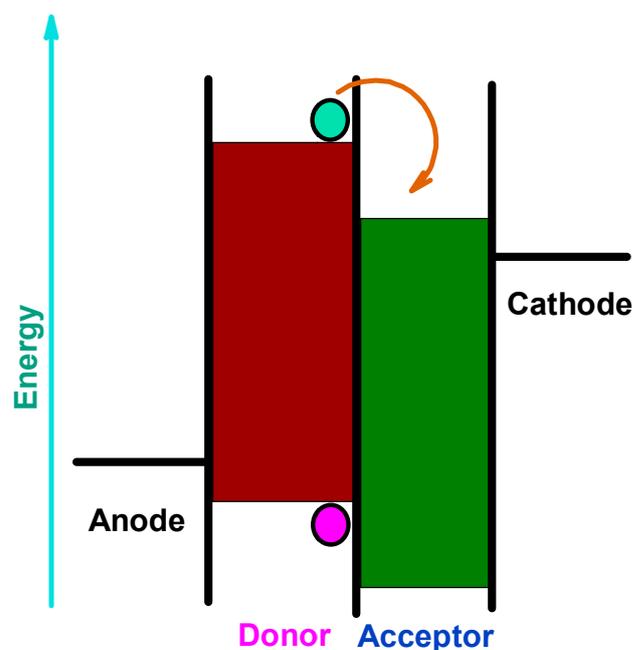


Figure 3. Energy levels and charge separation in an organic solar cell

In applications of highly soluble and efficient new low band gap type of organic materials are recommended because of their good morphology, tuneable structure and high molar absorption coefficient. Research on organic solar cell has developed during last 30 years, but especially last 10 years since it has attracted many scientific and economic interest according to increasing efficiency (Hoppe and SerdarSariciftci, 2004). This interest has become tremendously high due to exploring new type of material and improved engineering in synthesis and application. Inorganic materials have been used for photovoltaic having high yield, but there has been enormous effort on organic materials (such as small organic molecules, semiconducting polymers) having relatively easy preparation (Chanberlain, 1983; Wöhrle and Meissner, 1991; Peumans *et al.*, 2003). Most of the organic semiconductors are hole conductors having an optical band gap around 2 eV, which is higher than silicon which limits the harvesting of solar spectrum. Nevertheless, the potential synthesis and application of organic semiconductor materials are higher than inorganics, having high molar absorption coefficients, absorption in relatively broader solar spectrum (from UV to near IR), easier preparation, lower toxicity and higher environmental friendliness, lower cost and higher flexibility for modifications via chemical synthesis. The first generation of organic photovoltaic solar cells was based on single organic layers having a sandwich arrangement between two metals electrodes having different work functions (Chanberlain, 1983; Wöhrle and Meissner, 1991). First reported power conversion efficiencies were generally low (in range of  $10^{-3}$  to  $10^{-2}$  %), but in merocyanine dyes efficiencies reached 0.7 % (Morel *et al.*, 1978; Gosh and T. Feng, *et al.*). The next breakthrough was achieved by introducing the bilayer heterojunction concept having two organic layers with specific electron or hole transport properties arranged between two electrodes (Hoppe and SerdarSariciftci, 2004). Tang reported about 1% power conversion efficiency for bilayer type (a phtalocyanine derivative as p-type and a perylene derivative as n-type semiconductor) sandwiched between a transparent conducting oxide and semitransparent metal electrode (Tang,

1986). Hiramoto and co-workers introduced the concept and first work of organic tandem cell structure by stacking two heterojunction devices (Hiramoto *et al.*, 1990). They also developed a three layer p-i-n like structure with a co-deposited interlayer between p-type (hole conducting) and n-type (electron conducting) layers (Hiramoto *et al.*, 1991 & 1992). Also, in same years conjugated polymer field developed rapidly and first single layer devices based on new developed materials were reported (Karg *et al.*, 1993; Marks *et al.*, 1994; Yu *et al.*, 1994; Antoniadis *et al.*, 1994). Reported results showed less than 0.1% power conversion efficiency. The bulk heterojunction type having similarities to the coevaporated molecular structures of Hiramoto (Hiramoto *et al.*, 1991 & 1992) was introduced by blending two polymers having donor and acceptor properties (Yu and Heeger, 1995; Halls *et al.*, 1995; Tada *et al.*, 1997). There is a wide research field of dye sensitized, electrochemical solar cells having conceptually similarities to the bulk heterojunction type of organic solar cell. The first attempts in this field were largely developed and improved by the Gratzel group (Tributsch and Calvin, 1971; Tributsch, 1972; Osa and Fujihira, 1976; Fujihira *et al.*, 1977; Tsubomura *et al.*, 1978; Matsumura *et al.*, 1969; O'Regan and Gratzel, 1991).

The application of printing technology as a fabrication tool for organic solar cells indicates the potential of these novel materials for future light-activated power plastic sources. Among other printing technologies recently implemented for the fabrication of organic electronic devices, such as gravure (Shaheen *et al.*, 2001) or screen printing (Tuomikoski, 2006), the inkjet printing technique is very promising due to the compatibility with various substrates because the ink material is transferred from the writing head to the substrate without direct contact with the surface (Tuomikoski, 2006). Defined areas can be precisely printed with high resolution very easily by drop on demand (DOD) and thus, a postpatterning of the coated layer can be eliminated. The DOD technology provides easy patterning of the functional layers which is necessary concerning the interconnection of solar cell modules, where adjacent cells are electrically connected to each other in series. Recently certified 5.21% power conversion efficiency (PCE) large area organic solar cell have been demonstrated from Konarka Technologies (Certified by National Renewable Energy Laboratory (NREL) from Nov 2006) and identification of suitable printing methods for production of organic photovoltaics is regarded as the next important milestone.

In the case of polymer: fullerene blends the morphology formation for the inkjet printing process is fundamentally different to the film forming after spin coating process. Therefore, inkjet printing of organic bulk heterojunction solar cells requires completely novel approaches and skill sets compared to the current state of the art. In particular inkjet printing, the common solvents (Shaheen, 2001; Padinger *et al.*, 2003; Waldauf *et al.*, 2006; Schilinsky *et al.*, 2006) drying conditions (Kim, 2005; Ma *et al.*, 2005; Reyes-Reyes, 2005; Li *et al.*, 2005; Kim, 2006; Schilinsky *et al.*, 2006) and chemical properties for regioregular (RR) poly(3-hexylthiophene) (P3HT):methanofullerene (PCBM) (Kim, 2006 & 2007; Schilinsky *et al.*, 2006) solar cells should be in adequate nanomorphology for the inkjet printing technology. Besides the choice of the solvent and the processing conditions, the morphological properties of an inkjet printed P3HT:PCBM active layer demands proper design of the

regioregularity (RR) of the polymer or small molecule donors. The RR needs to be chosen to extend the gelation time of the RR-P3HT:PCBM blend, and the choice of the solvent formulation should allow a higher drying rate of the wet bulk with a coating at low deposition temperatures. Recently, a power conversion efficiency (PCE) of 3.5% has been achieved for improved solar cell device performance (Hoth *et al.*, 2007; Hoth *et al.*, 2008). PCE can be further increased with optimized critical parameters for the production of highly efficient organic solar cells.

## MATERIALS AND METHODS

### Research Project Design

In this project, triarylamine derivatived organic small molecules will be synthesized via Suzuki Coupling, Knoevenagel reactions and organic solar cells (OSC) with highly soluble novel donor materials will be produced by using inkjet method and then it will be shown how the physical properties of the materials and which mechanisms effect the performance and efficiency of these solar cells. To do this, the electrical characterization, optical and microstructure properties of these produced organic solar cells will be investigated by means of NMR spectra ( $^1\text{H}$  and  $^{13}\text{C}$ ), IR UV-Vis spectra, Photoluminescence, Cyclic voltammetry, SEM, AFM will be used for surface characterization. Moreover, J-V characteristic curves and the efficiency of these developed organic solar cells will be determined using solar simulators.

### Synthesis of Alkoxy Derivative of Triarylamine

#### First Step

Synthesis of 1-(hexyloxy)-4-iodophenol. In a round bottomed flask a mixture of 4-iodophenol (8.8g, 40mmol), potassium carbonate (5.6g, 40mmol), 18-Crown-6 (1g, 4mmol), acetone (100mL) 1-bromohexane (6.6g, 40mmol) were added and refluxed with stirring overnight. Reaction controlled and ended with TLC, cooled down to room temperature, filtered and extracted with diethylether (20mL) and water (20mL). Organic phase will be separated, dried over sodium sulphate and solvent evaporated by rotary evaporator. The crude product will be purified by column chromatography (dichloromethane/hexane: 1/1, V/V) to afford colourless oil (91%, yield).

#### Second Step

Synthesis of (4-bromophenyl) bis [4-(hexyloxy)phenyl]amine. In a round bottomed flask a mixture of CuI (0.2g, 1mmol) the phenantroline (0.18g, 1mmol) were added and dissolved in toluene (10mL). Dean-Stark apparatus reflux condenser were set and reaction mixture will be stirred for half an hour. 1-(hexyloxy) - iodobenzene (5g, 16mmol), 4-bromoaniline (1.65g, 9.6mmol), potassium hydroxide (4.8g, 77mmol) and toluene (20mL) were added, the mixture will be refluxed with stirring overnight. Reaction will be controlled and ended with TLC, cooled to the room temperature, filtered over celite and washed with dichloromethane. Reaction mixture extracted with dichloromethane (3x20mL) and water (3x20mL). Organic phase will be separated, dried over sodium sulphate and solvent evaporated by rotary evaporator.

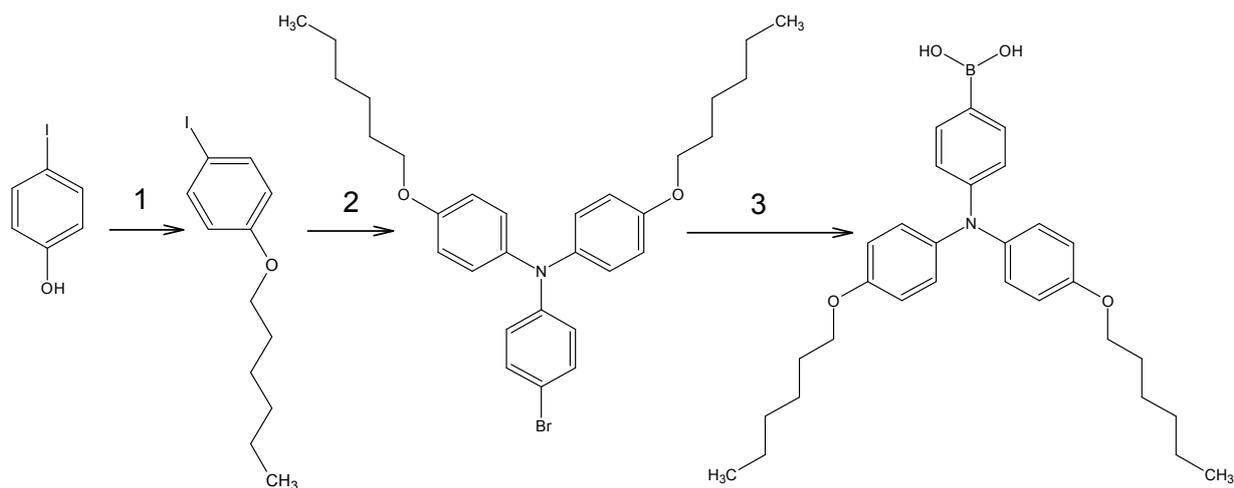


Figure 4. Synthesis of the highly soluble donor compound

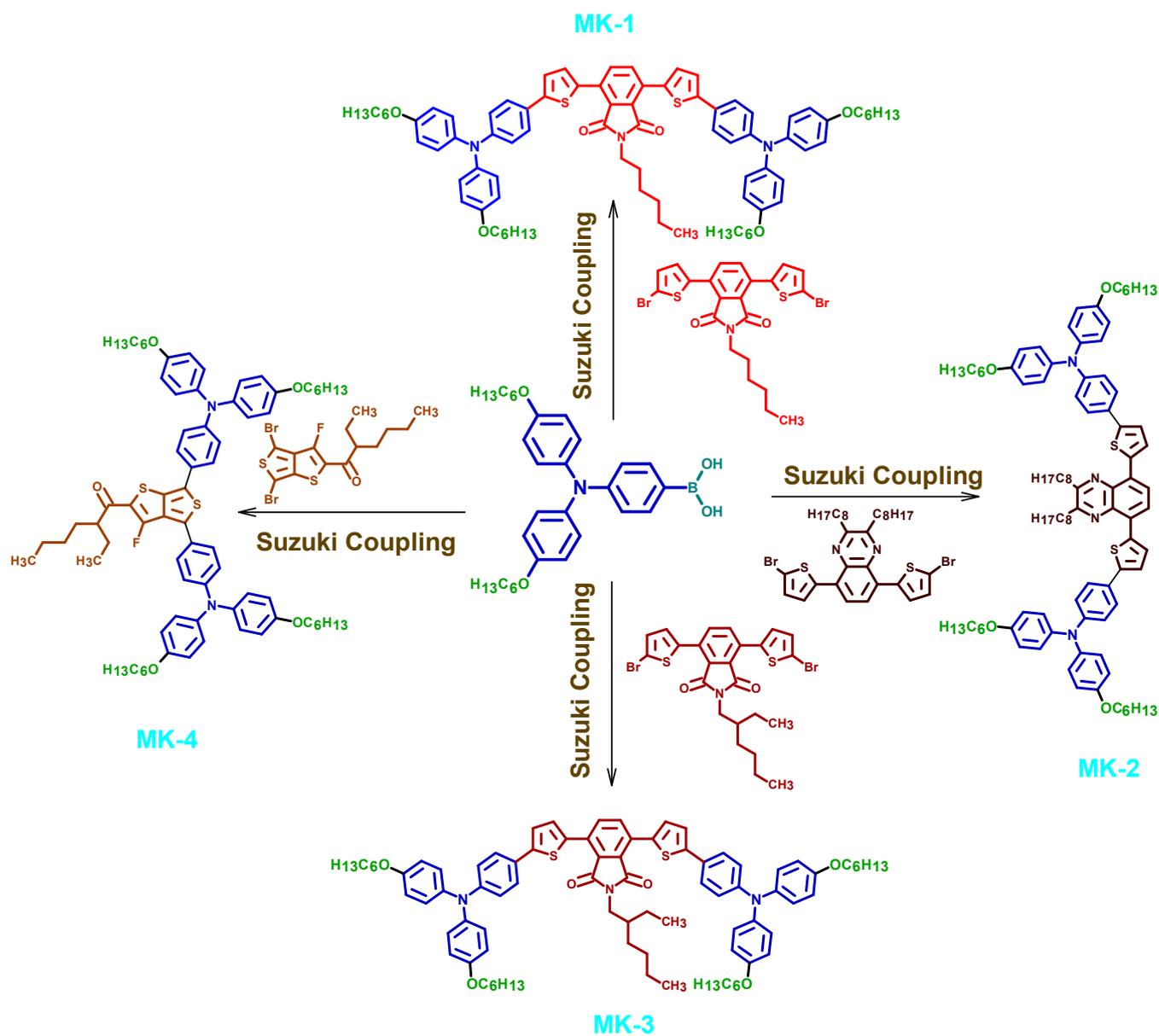


Figure 6. Synthesis of the target low band gap small molecules.

The crude product will be purified by column chromatography (dichloromethane/hexane: 1/4, V/V) on silica gel to yield yellow oil (66% yield).

### Third Step

Synthesis of 4-([4-(hexyloxy)phenyl]amino)phenyl Boronic acid. A round bottomed flask will be vacuumed and given argon which provides isolated atmosphere. (4-bromophenyl) bis [4-(hexyloxy)phenyl]amine (3.8g, 7.3mmol) will be dissolved with dry THF (10mL) and added to flask, temperature will be set to -80°C with acetone and dry ice, n-buthyl lithium (3.75mL, 7.25mmol) will be added drop wise carefully and stirred for half an hour. Trimethyl borate (8.4mL, 72.6mmol) will be added drop wise, respectively. Reaction will be controlled and ended with TLC. The residue will be extracted with diethylether (3x30mL) ve 1M hydrochloric acid aqueous solution (3x30mL). Organic phase will be separated, dried over sodium sulphate and solvent evaporated by rotary evaporator. The crude product will be purified by column chromatography (ethyl acetate /hexane: 3/1, V/V) on silica gel to afford white solid (74% yield).

### Fabrication of Solar Cells: Inkjet printing Technique

Mostly traditional methods used in the production of solar cells causes a rise in their production cost. The usage of inkjet method which is very cheap and whose application is very simple in the production of these PV and OSC cells will be very effective in the reduction of the energy costs. At the same time, it is foreseen that application of organic solar cells by using this inkjet technique is an easier, faster, low cost, and established technology. It allows printing on flexible substrates in ambient conditions with digital patterning options in mass production (up to 150 m<sup>2</sup>/h).



Figure 7. Ink jet (inkjet) material spraying device

PCE for highly efficient organic solar cells by printing can be further increased with optimized critical parameters such as the inkjet latency time (effect of gelation), the inkjet printing table temperature, the effect of drying related to both inkjet table temperature and solvents and the effect of the chemical properties of the polymer donor. For scientific and technological challenges for highly efficient inkjet printed organic solar cells, all the above parameters are strongly affecting the morphology and film formation of inkjet printed organic BHJ solar cells with equivalent cells made by other more conventional processing methods like spin coating.

### Value to this project

The value of this research studies in a project to find alternative energy with respect to oil. This is optional and not required for the following reasons, most major energy companies in the world search to discover new energy equal to the amount of oil they are producing for the last few years. They estimate vary from 50 to 150 years before we run out of oil. Also the uses of oil is not friendly with the environment, where the main disadvantages of using oil is a carbon based fuel and the primary way it is used is to burn it, releasing more than its weight in CO<sub>2</sub> because of the added oxygen. CO<sub>2</sub> is a greenhouse gas and is expected by most scientists to be a cause of global warming. For this reasons, industrial expansion in various fields needs to find a clean alternative energy does not badly affect their use on the environment at the same time to produce this energy (solar energy) from in expensive materials economically also. In our region we have abundant of sunshine throughout the year so we can produce the solar energy as a big strategically project and economically to export it besides oil. Also solar energy is renewable energy source meaning it is being constantly replenished and cannot be depleted like this is the case with fossil fuels. As long as Sun keeps shining solar energy will be available to us.

The potential positive impacts on the economy and society at large is very wide. Aside from the obvious financial benefits posed by solar energy for those who there are other advantages available as well. Face it, solar energy is definitely the future trend of energy. Nowadays, many households have converted their home to be powered solely by solar power, reaping all the advantages offered by the sun. So we do not need to change our home because our country is very wealthy by the sunshine but we have to think very well how to utilize this energy which god gave it to us. Moreover, there no remind disadvantages for solar energy just the problem is still the cost of the solar generation technology very expensive. Therefore the main course of this investigation to generate solar energy with low cost

### The advantages offered by the sun are

- That the key reason that most households convert their power source to solar energy is to cut down their electrical bill because the electrical usage generated from the sun is free. By converting as many home appliances as possible to use solar energy, you can save a significant savings in your utilities expenses.
- It is a renewable energy source: typical electricity is generated from fossil fuel that will run out after a while. Solar energy is a good alternative to replace fossil fuel as the major energy source because solar power is renewable at absolutely no cost to supply energy infinitely.
- Environment friendly, the world pollution is getting worse. Any effort that can reduce the pollution to the environment helps to save the earth. Solar panels are able to harness the energy from the sun and convert it to electricity. Therefore, the use of solar panels is environment friendly, harmless to the environment, clean, environmentally friendly source of energy
- Low / no maintenance needed, once you have installed the solar power system, it can last twenty to thirty years without major maintenance needed. You may need to

do system check once a year, just to make sure everything is performing as it should. Since it requires very minimum maintenance cost, your cost should be minimal. These days. Here is the list featuring the most important factors that make solar energy a „good energy source. For that rezones it will be the major energy source for future and it will be the most popular energy source in the world so it has to starting today.

Economically, solar energy can help improve our energy independence and energy security by reducing the need for oil and natural gas as fuel for transportation, which is possible to assist in the provision of oil and gas as important elements of rich materials (oil) that utilize in various industries in our lives such as:

- The oil excellent source of organic molecules for building plastics, medicines, rubber, fiber, etc.
- Can withstand high heats without breakdown making it useful as lubricants like motor oil and grease.
- Residuals make excellent surface for asphalt roads and waterproof roofing materials.
- Certain components make excellent solvents for paint, industrial use etc.
- Other components (propane, butane) make excellent compact source of portable cooking fuel and heating in areas that do not have infrastructure for natural gas delivery.
- Also, natural gas is used to make fertilizers used in agriculture and household detergents.
- The oil industry has been a source of much advanced technology and many new products that have changed our lives for the better as the product materials not just as source of energy.

But the disadvantages of fossil fuels have bad side effect on our society and natural it can be increased the green house effect, and our society and our life can be influenced if we use it for generating energy besides produce oil materials also. In contrast as we remembered above the solar energy is clean and environmentally friendly source of energy that doesn't contribute to climate change. And the benefits of solar power are becoming increasingly evident. Whether it's to save money or to help the environment, thousands of homeowners and businesses are choosing to invest in solar power.

#### **The following are examples of the many benefits in any economic**

The Solar energy industry creates plenty new jobs that can give huge boost to our economy. Solar energy is extremely abundant source of energy with almost unlimited potential. Solar energy is free source of energy because nobody owns the Sun. Adding solar panels improves the value of our properties. Adding solar panels improves the value of our society. Solar panels are very silent and do not create noise pollution like some wind turbines do. In addition to; Solar energy can help electrification of many rural, mountains and desert areas, particularly in developing world. Solar panels have very good lifespan of 20+ years. Solar panel prices have been constantly dropping in the last five years. Solar panels require very little maintenance. Solar energy industry is the fastest growing industry in the nation giving plenty of business opportunities to young people. Solar panels do not lose much efficiency over

the years and can be recycled. Also, benefits for education and training of Saudi students; the career development of researchers and people employed within the solar energy industry have very good salaries. Solar power engineer, for instance, can earn much more money. It is worth mentioning in this section the targeted end users and the suitable mechanisms for utilization and implementation of the project deliverables. Moreover; investing in solar allows researchers to own their power plant in their countries, instead of renting power at an inflated price. It allows us to lock in our electric rate at a fraction of today's electric costs, and it makes our immune from future rate hikes. It's also worth noting that investing in renewable energy such as solar power reduces the nation's utilities of fossil fuels such as oils and natural gas in order to keep our life healthy and save and our environment cleans and spend on the pollutions. The economic feasibility and proceeds; the main purpose of this research is to find out the best way to achieve this project in easier mechanism from cheapest cost materials in order to achieve high economic feasibility with a good outcome at the same time, which we look to export the product of suitable solar energy besides the oil products to the whole world.

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