

# Fabrication of Organic Solar Cells based on Photosensitive Small Molecules and Study of Electron Acceptor Layer Effect on Efficiency

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**Abstract.** We have designed and synthesized an efficient and novel photosensitive two small organic molecules with different lengths of methine units, cyano groups as the electron acceptor units, and amino groups as the electron donor units. Compound 1 was synthesized from benzaldehyde, malononitrile and hydrazine hydrate and benzaldehyde whereas compound 2 was synthesized from benzaldehyde, Dimedone and hydrazine hydrate and their thermal, photovoltaic and surface properties were studied. Then these small molecules were utilized for development of organic solar cells in FTO: ZnO: Organic compound: Electrolyte: Pt electrode pattern.

**Keywords:** Organic solar cells (OSCs), zinc oxide (ZnO), titanium Oxide (TiO<sub>2</sub>), electrolyte, efficiency.

## 1 Introduction

Organic solar cells (OSCs) have attracted significant interest because of their great potential to become green energy source with large-area, light-weight, superior mechanical flexibility, and low cost processes by roll-to-roll manufacturing [1-4]. Zinc oxide (ZnO) is a versatile semiconductor material, with wide range of applications in photo electrochemical cells [5], lasers [6], and other electrical devices [7, 8]. ZnO is a promising candidate for contact layers in next-generation thin-film photovoltaics because it is a low-cost, non-toxic, earth-abundant material with multiple solution deposition routes to the formation of thin films [9]. ZnO is a wide band gap semiconductor with an energy gap of 3.3 eV and a conduction band edge of 4.3 eV. This band edge is sufficiently high to extract electrons from typical donor and acceptor molecules and/or polymers [10]. There are many methods used for the ZnO deposition like spin coating, atomic layer deposition, screen printing, nano-imprinting, pulsed laser deposition, spin-cast and spray coating etc [10-14].

Diego Barrera et al reported thermal annealing of P<sub>3</sub>H<sub>2</sub>T:PCBM bulk heterojunctions (BHJs) on top of a commonly used sol-gel ZnO electron transport layer leading to the formation of PCBM clusters [15]. Fabrication of a bilayer hybrid organic solar cell with P3HT as the donor and ZnO as the acceptor (ITO/ZnO/P3HT/Au) having the power conversion efficiency of the self-assembled monolayer modified device was approximately 60% higher than that of the untreated device [16]. Synergistic effect of dual interfacial modifications with room-temperature-grown epitaxial ZnO and adsorbed indoline dye for ZnO nanorod array/P3HT hybrid solar cell giving efficiency of 1.16% has been reported [17]. The P3HT:PCBM-based flexible organic solar cells (FOSCs) fabricated by brush-painting processes have been reported to have a power conversion efficiency of 2.055% [18]. The synthesis of poly(3-hexylthiophene) (P3HT)/HA ZnO nanocomposite by in situ polymerization has been reported with the solar to electric energy conversion efficiency of 0.1238 % [19].

In continuation of our research work in synthesis [20-25] and solar cell [26], herein we report the synthesis of 5-amino-3-phenyl-2, 3-dihydro-1H-pyrazole-4-carbonitrile (1) and 6, 6-dimethyl-3-phenyl-2,3,6,7-tetrahydro-1H-indazol-4(5H)-one (2) organic compounds. Their optical, thermal and photovoltaic properties are investigated. A power efficiency efficiencies upto 0.077% has been obtained under simulated solar irradiation.

## 2 Experimental

### 2.1 Chemicals and Instrumentations

Dimedone was purchased from sd-fine chem limited, India. Benzaldehyde and malononitrile were purchased from Spectrochem chemicals. Ethylene glycol was purchased from Fischer scientific and hydrazine hydrate was purchased from Sigma Aldrich.

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Bruker Advance II spectrometer operating at 300 and 75 MHz, respectively. Liquid Chromatography-High resolution mass (LC-HR-MS) spectra were recorded on a 6550 iFunnel QTOF LC-MS/MS Make-Agilent Technologies 1290 Infinity Binary Pump. The thermogravimetric analyses (TGA) were carried out on a Perkin Elmer 4000 Instrument under purified nitrogen gas flow with a 10°C min<sup>-1</sup> heating rate. Surface roughness and morphology of thin films were characterized by Field Emission-Scanning Electron Microscopy (FE-SEM) on an S-4800 instrument from Hitachi, Japan, operated at 10 kV (Kilo Volt) and elemental analysis was performed by the EDS unit coupled with the FE-SEM unit. Film thicknesses were measured by using a thickness profiler DEKTAK-150 profilometer for area 1000 nm. The current density–voltage (J–V) characteristics of the organic solar cells (OSCs) were measured under AM1.5G (100mWcm<sup>2</sup>) illumination which was provided by a 3A grade solar simulator (Newport, USA, 94043A, calibrated with a standard crystalline silicon solar cell).

### 2.2 Synthesis

5-amino-3-phenyl-2,3-dihydro-1H-pyrazole-4-carbonitrile (1)

A mixture of benzaldehyde (5mmol), malononitrile (5mmol), hydrazine hydrate (99%) (5mmol) and 20mol% Al<sub>2</sub>O<sub>3</sub> in 5ml ethylene glycol was refluxed at 100-120°C for 3 hrs. After cooling to room temperature, the reaction mixture was poured in ice cold water, a yellow solid precipitated out which was then filtered. The obtained crude product was then purified by silica gel column chromatography using ethyl acetate and hexane to give an orange solid product.



Yield: 90.39%

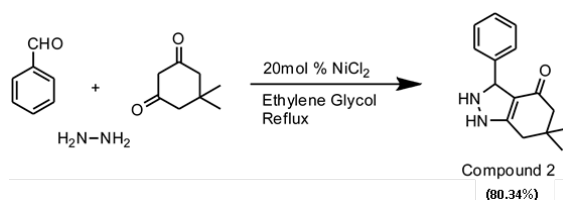
<sup>1</sup>H NMR (300MHz, DMSO): 4.297-4.35 (s, 2H), 5.554-5.67 (s, 1H), 6.755-6.80 (d, 2H), 7.440-7.64 (m, 3H), 8.297-8.50 (s, 2H)

<sup>13</sup>C NMR (75MHz, DMSO): 70.7, 73.9, 83.2, 97.5, 127.6, 127.9, 128.4, 129.3, 129.8, 133.6, 133.9, 160.3

GC-HR-MS: Calculated for C<sub>10</sub>H<sub>10</sub>N<sub>4</sub> 186.0887; found for ([C<sub>10</sub>H<sub>10</sub>N<sub>4</sub>]+H) 187.096

6,6-dimethyl-3-phenyl-2,3,6,7-tetrahydro-1H-indazol-4(5H)-one (2)

A mixture of benzaldehyde (5mmol), dimedone (5mmol), hydrazine hydrate (99%) (5mmol) and 20mol% NiCl<sub>2</sub> in 5ml ethylene glycol was refluxed at 100-120° C for 5 hrs. After cooling to room temperature, the reaction mixture was poured in ice cold water, a yellow solid precipitated out which was then filtered. The obtained crude product was then purified by silica gel column chromatography using ethyl acetate and hexane to give a yellow solid product.



Yield: 80.34%

$^1\text{H}$  NMR (300MHz, DMSO): 0.93-1.91 (s, 6H), 2.07-2.49 (s, 2H), 2.50-2.77 (s, 2H), 4.65 (m, 3H), 7.30-7.594 (m, 3H), 7.73-7.79 (d, 2H)

$^{13}\text{C}$  NMR (75MHz, DMSO): 20.7, 27.5, 30.9, 62.4, 126.8, 127.9, 128.5, 129.6, 134.1, 161.1, 171.7

GC-HR-MS: calculated for  $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}$  242.1409; found for  $([\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}] + \text{H})$  243.1476

### 2.3 Fabrication of Solar Cell Devices

Solar cells were fabricated on pre-patterned Fluorine doped Tin Oxide (FTO) ultrasonically cleaned with acetone, toluene, methanol, and isopropyl alcohol subsequently. Onto the FTO glass, acceptor layer of ZnO film was coated by SILAR (Successive Ionic Layer Adsorption and Reaction) technique shown in Figure 1. For SILAR technique, initially 50 mL of 0.1M  $\text{Zn}(\text{NO}_3)_2$  was prepared by dissolving appropriate amount of zinc nitrate in 50 mL distilled water. Similarly, 0.2M of NaOH solution was prepared. The pre-clean FTO glass was dipped into the solution of 0.1M  $\text{Zn}(\text{NO}_3)_2$  for 10 second then rinsed with distilled water and finally immersed in 0.2M of NaOH solution at  $60^\circ\text{C}$  for 10 second. Then again it was rinsed with distilled water for the completion of one cycle. Similarly, 150 cycles were performed for deposition of ZnO layer and then annealed at  $350^\circ\text{C}$  for 1 h in air. In some devices, acceptor layer  $\text{TiO}_2$  was used which was coated on FTO by dip coating method [26]. Then solutions of the organic compound 1 and compound 2 of concentrations 10 mM in ethanol were prepared and coated on FTO/ZnO by simple dipping method at  $60^\circ\text{C}$  for 10 minutes. Then electrolyte was introduced into OSCs. Two electrolytes were used containing 0.05M of  $\text{I}_2$  solution in Ethyl carbonate: Acetonitrile (80:20) and 0.5 M of tetra-n-butyl ammonium iodide, 0.05 M  $\text{I}_2$  in propylene carbonate: acetonitrile (6:4 volumes) and covered with platinum plate as counter electrode. Schematic representation of fabricated devices was shown in Figure 2.

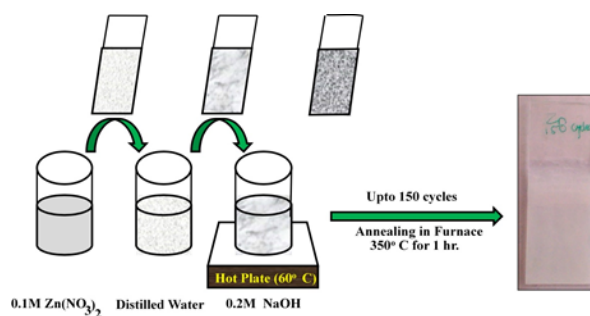
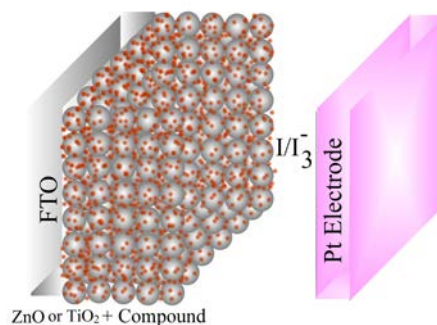


Figure 1. Coating of ZnO by SILAR technique

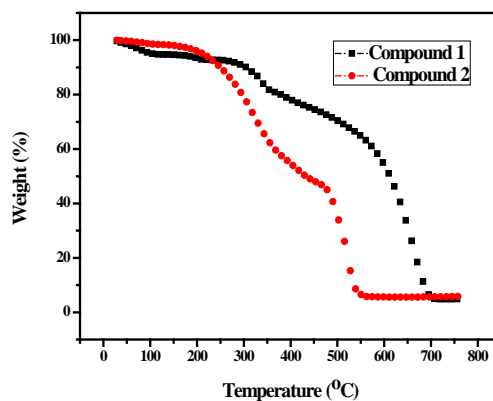


**Figure 2.** Schematic representation of fabricated devices

### 3 Result and Discussion

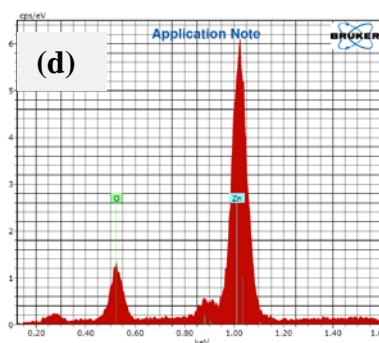
#### 3.1 Thermal Stability of Organic Compounds

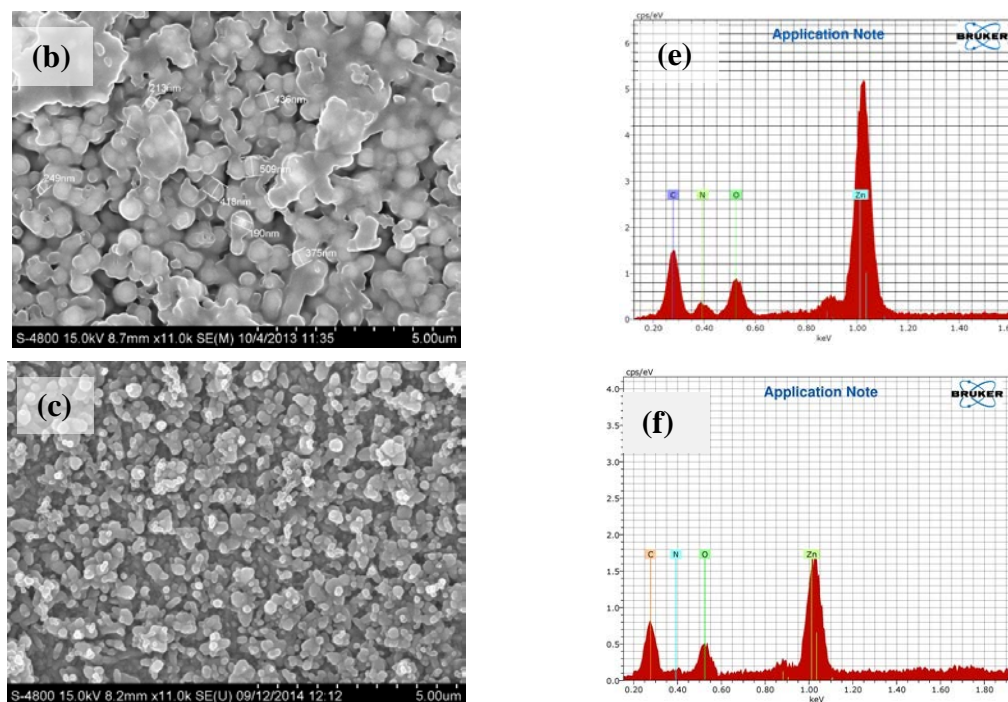
The thermal property of both compounds is investigated by thermogravimetric analysis (TGA). Compounds 1 and 2 exhibit good thermal stability with a decomposition temperature (5% weight loss) of 106°C and 242°C respectively in nitrogen shown in Figure 3.

**Figure 3.** TGA of Compound 1 and Compound 2

#### 3.2 Surface Characterization

FE-SEM is utilized to study the morphology of ZnO and ZnO/organic compound films. For this purpose, active layers were coated on glass plates using fabrication process described in section 2.3 and the morphology and EDX are shown in Figure 4. Figure (4a) shows nano-sized ZnO particles. Figure (4b) and (4c) show coating of organic compounds 1 and 2 on ZnO, respectively with increase in particle size, which confirm the successful coating of organic compounds over ZnO nanoparticles. EDX analysis (Figure 4) shows elemental composition of respective films and EDX spectra confirm the presence of respective elements in films.

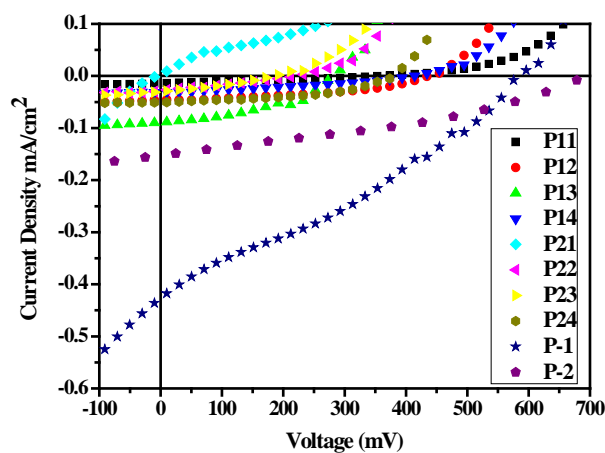




**Figure 4.** FE-SEM images of (a) ZnO film (b) Compound 1 coated on ZnO film (c) Compound 2 coated on ZnO film and EDS images of (d) ZnO film (e) Compound 1 coated on ZnO film (f) Compound 2 coated on ZnO film

### 3.3 Photovoltaic Properties

OSCs prepared with different device structures altering donor, acceptor and electrolyte composition and their photovoltaic characteristics are shown in Table 1. Different combinations of OSCs as FTO/acceptor/organic compound/electrolyte/Pt were prepared and tested under a simulated AM 1.5G illumination ( $100 \text{ mW/cm}^2$ ). Different compositions of acceptor and organic compounds were used to optimize the device performance and their current density vs. voltage ( $J-V$ ) curves are shown in Figure 5. Out of these different compositions, device P-1 has shown maximum efficiency of 0.077 % with 0.576 V as  $V_{oc}$  and  $0.418 \text{ mA/cm}^2$  as  $J_{sc}$ . From the results it can be concluded that small and simple organic compounds can be used in fabrication of OSCs.



**Figure 5.** The  $J-V$  characteristics of the different devices under the AM 1.5 illumination at  $100 \text{ mW/cm}^2$  condition

**Table 1.** Characteristics of different OSCs device performance

Device No.	Device Code	Device Material	Electrolyte	Voc (V)	Jsc (mA/cm <sup>2</sup> )	FF	% Efficiency ( $\eta$ )
1	P-1	FTO: ZnO (SILAR): Organic compound (P-1): Electrolyte: Pt electrode	0.05M I <sub>2</sub> solution in (80:20) Ethyl carbonate: Acetonitrile	0.575	0.418	0.320	0.077
2	P-2	FTO: ZnO (SILAR): Organic compound (P-2): Electrolyte: Pt electrode	0.05M I <sub>2</sub> solution in (80:20) Ethyl carbonate: Acetonitrile	0.693	0.152	0.367	0.039
3	P-11	FTO: ZnO (SILAR): Organic compound (P-1): Electrolyte: Pt electrode	0.5 M of tetra-n-butyl ammonium iodide, 0.05 M I <sub>2</sub> in propylene carbonate/acetonitrile (6:4 volumes)	0.353	0.014	0.302	0.001
4	P-12	FTO: ZnO (SILAR): ZnO(Dip coating): Organic compound (P-1): Electrolyte: Pt electrode	0.5 M of tetra-n-butyl ammonium iodide, 0.05 M I <sub>2</sub> in propylene carbonate/acetonitrile (6:4 volumes)	0.434	0.046	0.455	0.009
5	P-13	FTO: TiO <sub>2</sub> : Organic compound (P-1): Electrolyte: Pt electrode	0.5 M of tetra-n-butyl ammonium iodide, 0.05 M I <sub>2</sub> in propylene carbonate/acetonitrile (6:4 volumes)	0.299	0.088	0.454	0.012
6	P-14	FTO: ZnO (SILAR): TiO <sub>2</sub> : Organic compound (P-1): Electrolyte: Pt electrode	0.5 M of tetra-n-butyl ammonium iodide, 0.05 M I <sub>2</sub> in propylene carbonate/acetonitrile (6:4 volumes)	0.414	0.032	0.341	0.005
7	P-21	FTO: ZnO (SILAR): Organic compound (P-2): Electrolyte: Pt electrode	0.5 M of tetra-n-butyl ammonium iodide, 0.05 M I <sub>2</sub> in propylene carbonate/acetonitrile (6:4 volumes)	-	-	-	-
8	P-22	FTO: ZnO (SILAR): ZnO(Dip coating): Organic compound (P-2): Electrolyte: Pt electrode	0.5 M of tetra-n-butyl ammonium iodide, 0.05 M I <sub>2</sub> in propylene carbonate/acetonitrile (6:4 volumes)	0.232	0.026	0.292	0.002
9	P-23	FTO: TiO <sub>2</sub> : Organic compound (P-2): Electrolyte: Pt electrode	0.5 M of tetra-n-butyl ammonium iodide, 0.05 M I <sub>2</sub> in propylene carbonate/acetonitrile (6:4 volumes)	0.192	0.029	0.330	0.002
10	P-24	FTO: ZnO (SILAR): TiO <sub>2</sub> : Organic compound (P-2): Electrolyte: Pt electrode	0.5 M of tetra-n-butyl ammonium iodide, 0.05 M I <sub>2</sub> in propylene carbonate/acetonitrile (6:4 volumes)	0.394	0.051	0.457	0.009

## 4 Conclusion

We reported the synthesis and characterization of novel 5-amino-3-phenyl-2,3-dihydro-1H-pyrazole-4-carbonitrile and 6,6-dimethyl-3-phenyl-2,3,6,7-tetrahydro-1H-indazol-4(5H)-one compounds which have different lengths of methine units, cyano groups as the electron acceptor units, and amino groups as the electron donor units. These synthesized novel organic compounds were utilised for fabrication of organic solar cells in FTO: ZnO: Organic compound: Electrolyte: Pt electrode pattern producing up to 0.077% solar energy-to-electricity conversion efficiency ( $\eta$ ).

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