

Spectral Absorption Study in OPV Device

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We have studied the UV-Visible absorption spectrum of copper phthalocyanine (CuPc), zinc phthalocyanine (ZnPc) and Metal free phthalocyanine (Hydrogen Phthalocyanine - H₂Pc). We also study the effect of CuPc, ZuPc and H₂Pc as donar layer in (CuPc)/ fullerene (C₆₀), (ZuPc)/ (C₆₀) and (H₂Pc)/ (C₆₀) bilayer organic photovoltaic device (OPV) or Organic Solar Cell (OSCs), the enhancement of the overall performance of the OSCs with better spectral absorption. A variation in Efficiency in the device architecture has been observed. The variation in η is dominantly attributed to the increment in short circuit current density (J_{sc}) due to efficient photon harvesting by donor.

Keywords: Phthalocyanine, Bilayer OPV, UV-Visible spectrum.

1. INTRODUCTION

PV (Photo Voltaic) technology is a solar power technology where sun light is being directly converted into electricity. PV devices contain two electrodes with active materials sandwiched between them. When the sun light is made incident on a PV device (also known as solar cell) free electron and holes are generated via. absorption of incident light in the active layer/material that are transported and collected at respective electrodes. One of the important parameter that limits the efficiency of these devices is the mismatch between absorption spectrum of the materials and that of the terrestrial solar spectrum. The use of low band gap materials ($E_g < 1.8\text{eV}$) with the absorption spectrum spanning the whole visible and near infra red region is a viable method to expand the absorption spectrum of solar cells and therefore to increase their efficiency.

Phthalocyanine derivatives viz. CuPc, ZnPc and H₂Pc are very important small molecule donar materials for OPV devices. This paper focused on spectral coverage investigation carried out on the bi-layer small molecule CuPc, ZnPc and H₂Pc as electron donar material based OPV devices. Spectrophotometer is an instrument which measures and compares the incident, absorbed, reflected and transmitted light of a sample. There are three types of spectroscopic measurements; transmittance, absorbance and reflectance. Transmittance and absorbance measurements are made on transparent liquids and clear solids such as thin films and filters. Reflectance measurements are performed on the completely opaque or relatively thick samples. The ratio of the two light intensities, transmitted light (I) over the incident light (I_0) is known as the transmittance of the sample. And the absorbance is calculated by

$$A = -\log\left(\frac{I}{I_0}\right) \quad (1)$$

where I and I_0 are respectively the transmitted and incident light intensities. I_0 is also referred to the background or reference beam, which is measured with only the solvent or the substrate. Different materials absorb different wavelengths of light. Therefore, the wavelength of maximum absorption by a material is one of the characteristic properties of that material.

2. EXPERIMENT

2.1. Introduction of UV-Visible absorption

Shimadzu 2401PC spectrophotometer was used for the UV-visible absorption spectroscopic studies of the materials. The light emitted from the light sources is projected onto the monochromator. The output of the monochromator is allowed to pass through a stray light cutting filter and then the output of the filter is splitted into two parts by the beam chopper. One of the two parts serves as reference beam whereas second part serves as the sample beam. These beams pass through their respective cells/samples and strike the photomultiplier. After the reference and sample beams are picked up by the photomultiplier, the signals are converted into voltage signal. The absorption graph shows which particular wavelength is absorbed and which is transmitted by the sample [1, 2].

2.2. OPV Device formation (bi-layer configuration):-

The OPV devices have been fabricated on the pre-patterned and cleaned ITO (Indium Tin Oxide) coated glass substrate in the ITO/Donar layer/Acceptor layer/Al configuration as shown in Figure 1.

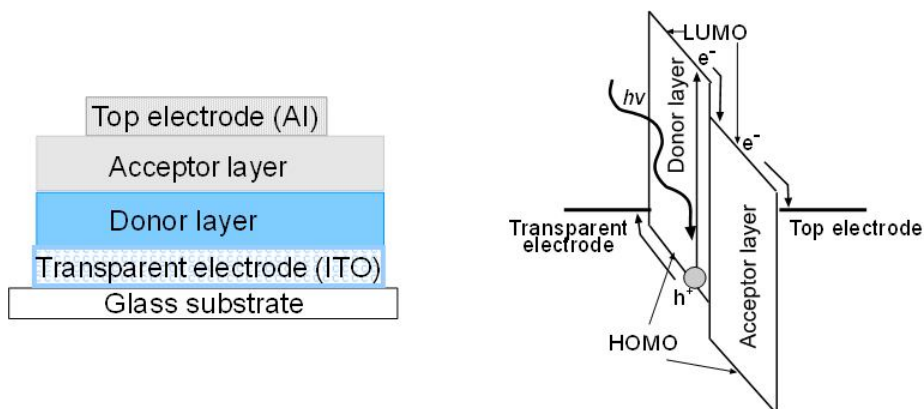


Fig.1: Bi- layer OSCs device structure

Prior to any deposition the ITO substrate were exposed to atmospheric plasma for 5min. The plasma treated substrates were transferred to a vacuum chamber where then film of different material were grown in the desired sequence. All the thin film was grown via thermal evaporation of the materials in vacuum at a base pressure of $\sim 4 \times 10^{-6}$ torr. Al (aluminium) cathode was deposited through shadow masks. The rate of evaporation of all materials was maintained at $\sim 0.1-1 \text{ \AA/s}$ by trial error methods. Thickness of different thin films was measured using a quartz crystal thickness monitor. The performance of OPV devices has been studied via. their *I-V* characteristics measured in dark and under illuminations using a Kithley 2420 source measure unit.

The devices fabricated for these studies are designated as **Devices 1, 2 and 3** and the configurations are as follows:

Device 1: ITO/H₂Pc (23nm)/C₆₀ (40nm)/BPhen (8nm)/Al (120nm).

Device 2: ITO/CuPc (20nm)/C₆₀ (40nm)/ BPhen (8nm)/ Al (120nm).

Device 3: ITO/ZnPc (25nm)/C₆₀ (37nm)/BPhen (8nm)/Al (120nm).

3. RESULT AND DISCUSSION

The phthalocyanine molecules may be unique with respect to structural, electrical and optical properties. Due to their intense colour, and high thermal and chemical stability, phthalocyanines were firstly employed as green and blue colorants in photographic, printing, plastic and textile industries [3]. Their intriguing optical and electrical properties [4] also enable them to be used in photoconductors, field-effect transistors, optical limiting materials, optical storage media and photovoltaic cells for energy conversion [5]. These materials exhibit good absorption in UV-visible region where absorption spectra possesses high energy Q bands which follows red shift when hydrogen in metal free phthalocyanine complex is replaced by Zn metal and blue shift for Cu metal.

The absorption spectrum of metal-free phthalocyanine and its metal derivatives (studied here), all showed the single absorption band at ~ 350 nm, which is characteristic of tetraazaporphins. Shimadzu 2401PC spectrophotometer was used for the UV-visible absorption spectroscopic studies of the materials. The visible spectra of the phthalocyanine with bivalent Cu and Zn metal complexes were very similar to one another, having a single, narrow, intense band in the 650-675 nm regions (see Fig.2). All absorption spectra exhibit four major bands marked as Q, B, N and C. The linear optical spectra of these compounds are dominated by two intense band, Q band (centred at around 670 nm) and B band (Soret band) in the near UV region (at ~ 340 nm), both correlated to π - π^* (bonding to anti-bonding) transitions [6]. The larger conjugated 18 π system makes the compounds absorb strongly in the red visible region (Q band) and in the near-ultraviolet region (Soret band), causing the characteristics blue-green colour. In CuPc material the Soret bands are taken as supporting evidence for explanation of structure in terms of molecular vibrations [11].

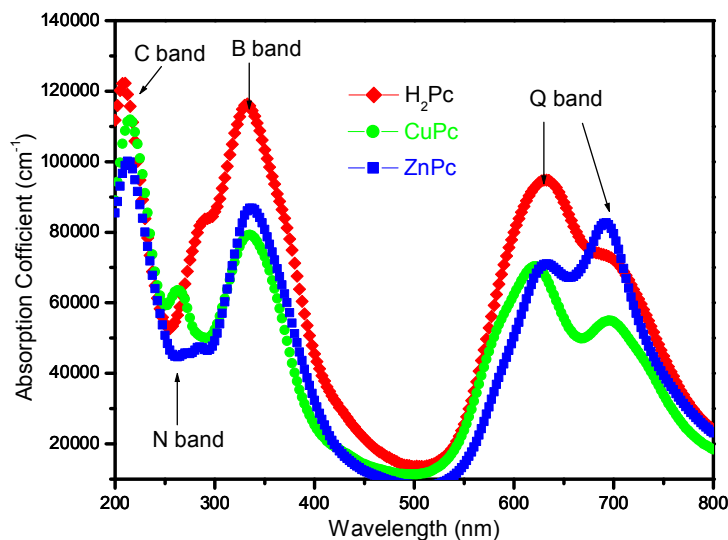


Fig. 2: UV-Visible spectra of H₂Pc, CuPc and ZnPc on quartz substrate.

In H₂Pc, CuPc and ZnPc there is no shift in position in B-band and C-bands is observed. The Q band (visible region) is split out in two distinct peaks. The high energy peak of the Q-band hand has been assigned to the first π - π^* transition on the phthalocyanine macrocycle [7]. The low energy peak of the Q-band has been explained as a second π - π^* transition, or attributed to the excitonic transition [8] or vibrational interval [9]. It is observed that by metal insertion we observe bathochromic shift in the sequence ZnPc < H₂Pc < CuPc in high energy Q-band. In low energy Q band there is no remarkable shift observed on H₂ replacement by Zn metal, however replacement of H₂ by Cu a hypsochromic shift was observed, which indicates that π - π^* transition requires more energy, this shows that the covalent character increases from Zn to Cu metal. Second absorption band due to π - π^* transition in the UV spectral region is B band. In H₂Pc, ZnPc and CuPc there is no shift in Soret band observed in all compounds and exhibits at \sim 336 nm. There is also a small peak (N band) which has been attributed to the charge transfer (CT) from sp_z mixing orbital to the electron system of the macrocyclic ring of phthalocyanine [8]. In ZnPc this N band appears to be at \sim 280 nm which is at higher wavelength than that in CuPc which requires high energy for charge transition from sp_z mixing orbital to the electron system of the macrocyclic ring of phthalocyanine. These absorption spectra occur in the high energy region of the Soret band (the N peak) also indicate the presence of d orbital associated with the central metal atom. It is thought that π - d transitions are involved and CuPc has partially occupied d orbital. In support in this explanation, Edwards and Gouterman pointed out that transitions involve d electrons of the central metal atom [10]. The C band is due to the d - π^* transition, which implies a broader d band. The absorption bands in the region of 275 nm to 217 nm are due to d - π^* transitions [7]. Similar behaviour of the absorption spectra has been obtained by some other workers as well for other metal-derivative phthalocyanines [7, 11].

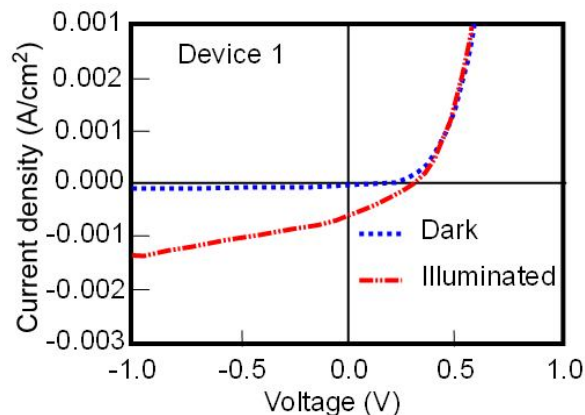


Fig.3: Dark and illuminated J-V characteristics of the Device 1 (under illumination intensity of $\sim 80 \text{ mW/cm}^2$).

To understand the effect of absorption on performance of OPV device we study only the current and voltage of different OPV devices in which these phthalocyanine used as donar material. The investigations were carried out on the optimized devices without interface layers. The optimized layer thicknesses/configuration for CuPc, H₂Pc and ZnPc based materials were found to be ITO/H₂Pc(23nm)/C₆₀(40nm)/Al (150nm) (**Device 1**), ITO/CuPc(20nm)/ C₆₀ (40nm)/Al(150nm) (**Device 2**) and ITO/ZnPc(25nm)/ C₆₀ (37nm)/Al(150nm) (**Device 3**), respectively.

The **Device 1** exhibited $J_{sc} = 0.58 \text{ mA/cm}^2$, $V_{oc} = 0.27 \text{ V}$, **Device 2** exhibited the $J_{sc} = 0.19 \text{ mA/cm}^2$, $V_{oc} = 0.35 \text{ V}$, and **Device 3** at room temperature exhibited $J_{sc} = 0.6 \text{ mA/cm}^2$, $V_{oc} = 0.31 \text{ V}$. The dark and illuminated J-V for device 1 is shown in Fig.3. The lower value of current in CuPc is due to the lower absorption in Q band of bathochromic shift in the sequence ZnPc < H₂Pc < CuPc in high energy Q-band. ZnPc has higher absorption coefficient of lower energy Q band then CuPc, in case of N band conditions are reversed CuPc has higher absorption coefficient then ZnPc. As first point for efficient solar cells is that the materials should be good absorber, because of one electron difference ZnPc is good absorber in red region and CuPc in UV region.

4. CONCLUSION

This enhancement in efficiency has been attributed to the enhanced absorption and improved photon harvesting in the device. The ZnPc material has higher absorption coefficient in Q band region compare to CuPc. Metal in Phthalocyanine changes the nature of bonding and morphology of material. Current density in OPV solar cell depends on the photon harvesting power of material and conductivity of excitons, free electron and hole and other parameters also which are under investigation. As such these results show that by the selection of suitable donar layer in organic active layer the efficiency of the OSCs can be enhanced further.

5. ACKNOWLEDGMENT

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