



Study of solvent dependence of Methyl Red and C₆₀ based organic photovoltaic devices

S. Saha, N.B. Manik *

Condensed Matter Physics Research Center, Department of Physics, Jadavpur University, Kolkata – 700032, India

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ABSTRACT

In this work, the effect of solvent on the photovoltaic properties of Methyl Red (MR) dye and C₆₀ based device has been reported. It can be assumed for a dye based photovoltaic device that there is an effect of solvent on the film morphology which controls the charge transport mechanism. To observe this effect of solvent on the film morphology two different solvents namely chlorobenzene and toluene are used to prepare the solutions of MR and C₆₀. The devices made with chlorobenzene and toluene solvents are termed as chlorobenzene cell and toluene cell respectively. For each solvent different devices are prepared by varying the weight ratio of MR and C₆₀. These cells are characterized through different photovoltaic measurements. Experimental data reveal that the photovoltaic response is higher in case of chlorobenzene cell than that of the toluene cell. The power conversion efficiency for toluene cell for a particular concentration of MR:C₆₀ is 0.781×10^{-7} whereas for chlorobenzene cell it is 1.026×10^{-5} . Maximum V_{oc} and J_{sc} obtained for toluene cell are 19.5 mV and 33.73 nA/cm² whereas for chlorobenzene cell these are 720 mV and 158.0 nA/cm² respectively. Scanning electron microscope images indicate the difference in nano-morphology and cluster sizes between the cells. The cluster size is quite large in case of toluene cell with comparison to chlorobenzene cell. From the transient photocurrent measurement it is observed that the charge transport process is quite faster in chlorobenzene cell which prevents excess recombination resulting in a higher efficiency in chlorobenzene cell.

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1. Introduction

Organic photovoltaic cells have attracted attention in the past few decades due to their ease of fabrication, large scale low cost-production in spite of its low power conversion efficiency compared to its inorganic counterpart [1–8]. The major goal of research in this area is to increase the power conversion efficiency. Use of different device structures, incorporation of nano particles, and selection of new dyes are the different techniques which are being used in this direction [9–11]. An encouraging breakthrough in realizing higher efficiencies has been achieved by mixing electron donor type polymers with suitable electron acceptors. The main progress in solar energy conversion efficiency has been achieved by introducing the bulk heterojunction concept [6,7,12] instead of bilayer structure [13,14] for the photoactive layer. The performance of the device is highly dependent on the complex nanoscale morphology of the film [15,16] which controls the charge transport properties of the device. It was evident that the charge carrier mobility measured in the devices is a function of the blend morphology [17]. Different morphologies

or the orientations of the molecules have a major role in the device performance. Different techniques are also used to control and regulate the morphology of the device. To prepare the film, organic dye is mixed with different solvents and depending on the nature of the solvents different morphological changes of the film are expected. As mentioned, device efficiency also depends on the morphological structure of the film. Some literatures [18–20] related to this work have inspired us to continue further work in this direction.

In this work we have studied the photovoltaic effect of Methyl Red (MR) and C₆₀ blended device. MR dye is one of the less reported dyes in photovoltaic mode. The role of C₆₀ is widely accepted as an acceptor in many literatures [21,22]. C₆₀ is insoluble in water but soluble in different organic solvents. In this work, two different solvents namely chlorobenzene and toluene have been chosen to prepare the solution since both MR dye and C₆₀ are soluble in these solvents. Solubility of C₆₀ in chlorobenzene and in toluene is 7.0 mg/mL and 2.8 mg/mL respectively [23]. The devices made with chlorobenzene and toluene solvents are termed as chlorobenzene cell and toluene cell respectively. The blends of MR dye and C₆₀ dissolved in chlorobenzene and toluene are spin coated on Indium Tin Oxide (ITO) coated glass plate and aluminum coated mylar (Al-M) sheet. Two electrodes are sandwiched together to prepare the device. For each solvent the weight ratios of MR:C₆₀ are varied to prepare different cells.

* Corresponding author. Tel.: +91 033 28673259; fax: +91 033 2837 1078.

E-mail address: nb_manik@yahoo.co.in (N.B. Manik).

2. Experimental details

2.1. Materials

MR dye was purchased from Finar Chemicals, Ahmedabad, India. 99.5% pure grade C_{60} and Poly Methyl Methacrylate (PMMA) were procured from Sigma-Aldrich. Fig. 1(a) and (b) shows the structures of MR dye and C_{60} . Toluene and chlorobenzene were procured from Merck Specialities Private Limited, Mumbai, India and Spectrochem Private Limited., Mumbai, India respectively. ITO coated glass is used as the front electrode and aluminum coated on mylar sheet abbreviated as Al-M is used as the back electrode. In our early work [24] it was observed that Al-M electrode shows better performance as a back electrode than ordinary Al. The reflectivity is quite higher in Al-M which enhances significantly the optical energy confinement within the film to ensure more absorption of light energy by the organic dye.

As mentioned earlier, MR dye has been chosen because it has a good optical response but in photovoltaic mode it is one of the less reported dyes [25]. MR with molecular formula NC_6H_4COOH (2-[4-(dimethylamino)phenylazo] benzoic acid) is a typical aromatic azo compound. Its color originates from absorbance in the visible region of the spectrum due to the delocalization of electrons in the benzene and azo groups forming a conjugated system. In addition to this it is a low cost and commonly available dye. Moreover, this dye is soluble in water as well as in organic solvents. The absorption spectra of MR dye and C_{60} separately in chlorobenzene and toluene solutions are measured and shown in Fig. 2(a) and (b) respectively. MR dye has the absorption peak at nearly 425 nm whereas the absorption peak occurs at nearly 250 nm for C_{60} .

Fig. 3(a) and (b) shows the structure of toluene and chlorobenzene. Chlorobenzene is an aryl halide. As we know aryl halides are unreactive as compared to alkyl halides because the halogen atom in these compounds is firmly attached and cannot be replaced by nucleophiles. Thus delocalization of electrons by resonance in aryl halides brings extra stability and double bond character between C–X bond where X is the halogen molecule. This reduces the bond length which makes the bond stronger than pure single bond. But for toluene the presence of methyl group makes it around 25 times more reactive than benzene.

2.2. Sample preparation

In a clean test tube 10 mL of chlorobenzene is taken and with it 1 g PMMA is mixed and stirred properly to get a clear solution. In this solution MR and C_{60} are mixed and stirred to get the solution of MR: C_{60} . Different solutions are prepared by varying the weight ratio of MR: C_{60} . Three different weight ratios of MR: C_{60} are prepared such as 1:1, 1:2 and 2:1. For 1:1 ratio, 1.0 mg of MR and 1.0 mg of C_{60} are taken to prepare the solution. For other two concentrations weight ratios of MR: C_{60} are varied accordingly. Solution is stirred well with a magnetic stirrer and left for 6 h to get proper solution.

To prepare the device this solution is spin coated on a pre cleaned ITO coated glass at a speed of 1500 rpm and the film is dried at a speed of 3500 rpm. The same solution is also deposited on Al-M electrode by the same technique. Both these electrodes are sandwiched

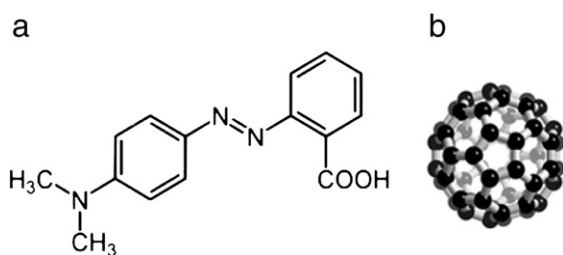


Fig. 1. Structures of Methyl Red (a) and C_{60} (b).

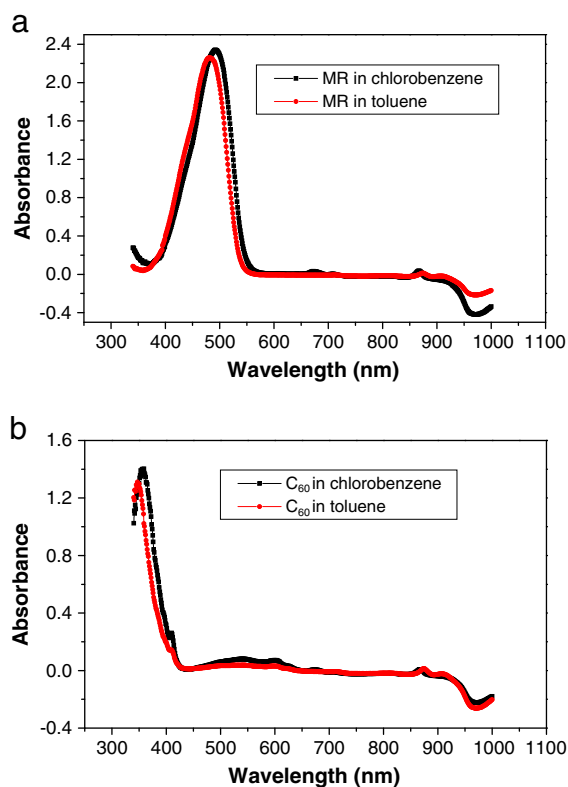


Fig. 2. Absorption spectra of (a) MR and (b) C_{60} dissolved separately in chlorobenzene and toluene.

together to form the chlorobenzene cell. The prepared cells are left in vacuum for 10 h to dry. Different devices are prepared in the same technique with chlorobenzene solution prepared for different concentrations of MR: C_{60} .

The similar technique is used to prepare the toluene cell. In a clean test tube 10 mL of toluene is taken and with it 1 g of PMMA is mixed and stirred. In this solution MR: C_{60} is added to prepare the solution. Different solutions are prepared of MR: C_{60} with weight ratios 1:1, 1:2 and 2:1. For 1:1 ratio 1 mg of MR and 1 mg of C_{60} are taken.

2.3. Measurements

Absorption spectra are measured with the help of Elico scanning mini spectrometer. Scanning electron microscopy (SEM) images are taken for both chlorobenzene and toluene cell. SEM analysis was performed on a JEOL field emission scanning electron microscope (JSM-6700F) operating at an accelerating voltage of 5 kV. X-ray diffraction (XRD) analysis of the cell was recorded by SEIFERT XRX 3000P using $Cu\ K\alpha$ ($\lambda = 1.5405\text{ \AA}$) as a radiation source, with a setting of 35 kV, 30 mA, 0.05° steps and a scan step time of 1 s. The image was recorded in reflection mode (Bragg–Brentano). With the prepared cells the dark current–voltage (I – V) characteristic is measured

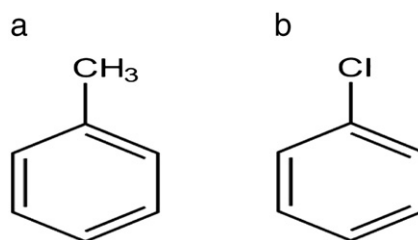


Fig. 3. Structure of toluene (a) and chlorobenzene (b) solvents.

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