

# Effect of C<sub>60</sub> on methyl red and crystal violet dye-doped photovoltaic device

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**Abstract** The potential of dye sensitization of organic photovoltaic devices has been investigated. The photoelectrical properties of such devices have been studied. With the help of spin-coating method, single layer and double layer structures are prepared with the help of both methyl red and crystal violet dye at a time. Methyl red and crystal violet dye are dispersed in polyvinyl alcohol used as an inert polymer binder and polyethylene oxide complexed with LiClO<sub>4</sub> ion salt as a solid electrolyte. Ethylene carbonate and propylene carbonate are used as plasticizers. A layer of this blend is sandwiched between two electrodes, one of which is indium tin oxide (ITO)-coated glass plate and another is Al electrodes. In this study, the use of a C<sub>60</sub> layer over the previously prepared blend is done. ITO-coated glass plate and Al electrodes are taken as counter electrodes. Use of C<sub>60</sub> molecule over the polymer blend in a heterojunction increased the efficiency of photovoltaic devices. In this type of device, the polymer blend acts as an electron donor to the second layers, whereas C<sub>60</sub> plays the role of an electron acceptor.

**Keywords** Photovoltaic device · Methyl red · Crystal violet · C<sub>60</sub>

## Introduction

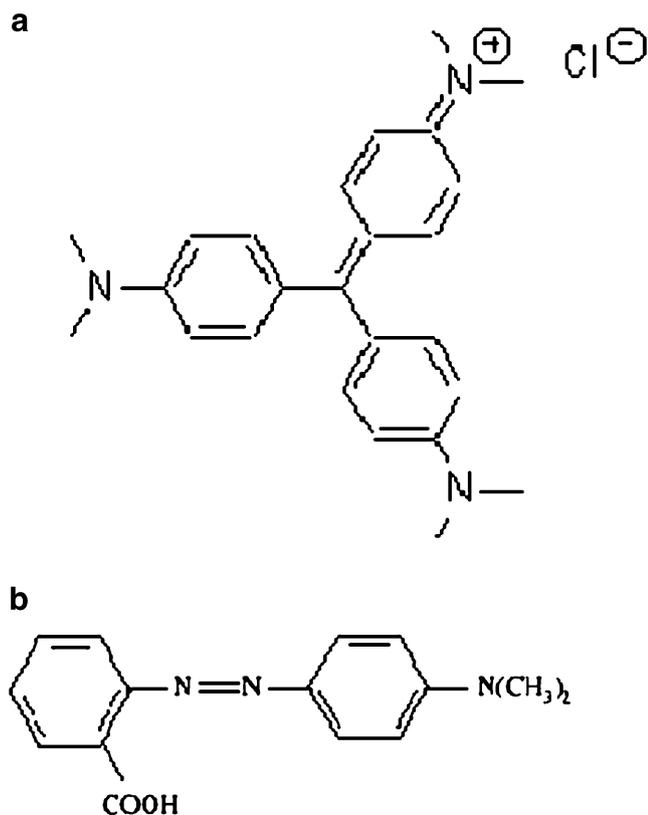
Photovoltaic devices based on organic materials have attracted attention in the recent years due to the possibility of producing large area and flexible devices. Several ap-

proaches for efficiency improvement have been proposed, especially with respect to geometry and materials synthesis. Nowadays, several research groups are able to obtain good light/current conversion efficiencies, motivating even more the research in the field. As single polymer layer device presents low efficiency due to the mechanism of charge generation and transport, the use of a C<sub>60</sub> (fullerene) layer (that has high electroaffinity value) onto the polymer in a heterojunction or mixture in the polymer film (blend) increased drastically the efficiency of the photovoltaic devices [1–5].

The low energy conversion efficiency of some photovoltaic devices is merely due to poor photogeneration excitons separation and low mobilities of holes or electrons in the organic thin films. To improve the dissociation of excitons and charge transport to the electrodes, the organic materials have been associated to the electron acceptors like fullerene [6–8]. This donor–acceptor network leads to an extremely rapid electron transfer from polymer to the C<sub>60</sub> that induces a high dissociation rate. To improve the photovoltaic properties of an organic solar cell, dye sensitization can be adopted. Addition of organic dyes could enhance the light absorption of organic materials. Thus, dye sensitization can be used to enlarge the spectral response of the photovoltaic devices. In the case of spin-coated films, the organic materials and dyes must be compatible in solution and in the solid state.

In this paper, we present a detailed study of the influence of C<sub>60</sub> layer over both cationic and anionic dye-based photoelectrochemical cell (PEC) structure. The PEC under study contains a blend made of crystal violet dye dispersed in transparent polyvinyl alcohol (PVA), polyethylene oxide (PEO) complexed with lithium perchlorate (LiClO<sub>4</sub>), ethylene carbonate (EC), and propylene carbonate (PC). Methyl red and crystal violet dye are used as an optical active material and is dispersed in PVA, which acts as an inert binder.

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**Fig. 1** Structure of **a** crystal violet dye and **b** methyl red

$\text{LiClO}_4$  is mixed with solid polymer matrix PEO to form the solid-state ionic conductor. The ionic conductivity of PEO/ $\text{LiClO}_4$  complexes are very low [9, 10]. The use of plasticizer is a common technique to enhance the ionic conductivity [11]. In this system, we have used EC that was dissolved in PC as plasticizers to enhance the mobility of the charge carriers. One solid film of this blend is sandwiched between transparent indium tin oxide (ITO)-coated glass plate and Al plate, which acts as two contact electrodes. Upon illumination from a light source, dye molecules absorb light and photocarriers are generated. These photocarriers are then separated by the external field generated at the contact of the electrodes. It is expected that the internal field produced by the redistribution of the ion species within the PEC [12–16] enhances the migration process of these photocarriers. The barrier potential in contacts of ITO and polymer materials is lowered [17, 18] due to the accumulation of these ion species near the respective electrodes leading to enhancement of charge injection through the metal polymer interface layer.

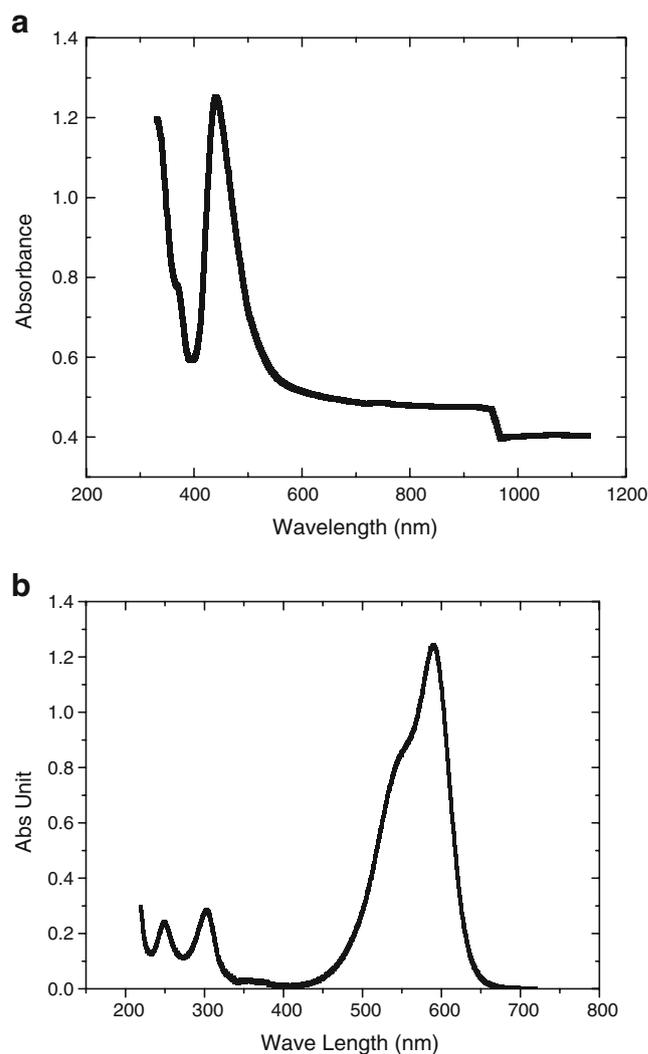
In this work, dark I–V characteristics and the photovoltaic currents with different intensity have been measured for comparison purpose. Improvement of photovoltaic parameters such as open circuit voltage,  $V_{oc}$ , short circuit current,  $I_{sc}$ , fill factor, FF, and conversion efficiency,  $\eta$ , has been observed, whereas ITO-coated glass plate and Al electrode are used as two contact electrodes.

The bilayer [19, 20] structure is more advantageous than the single layer structure for several reasons: Exciton splitting is enhanced by the D–A interface, the active region is extended to both the donor and the acceptor sides of the junction, and the transport of electrons and holes is separated into different materials reducing the recombination losses. In addition to this, by using two different semiconductors, the band gaps can in principle be tuned to match better the solar spectrum.

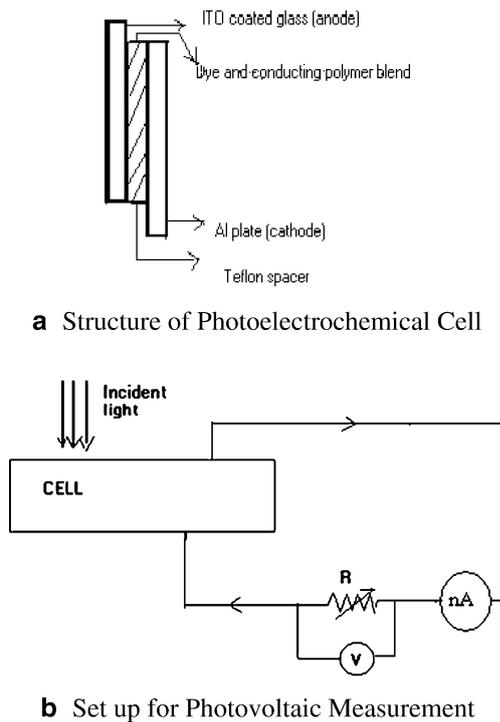
## Experimental

### Sample preparation

The structure of the dye, methyl red (Fluka), having the absorption peak at 440 nm that corresponds to an optical band gap of the order of 2.82 eV, and crystal violet (BDH,



**Fig. 2** Absorption spectra of **a** MR (curve A) and CV (curve B), **b** mixture of CV and MR

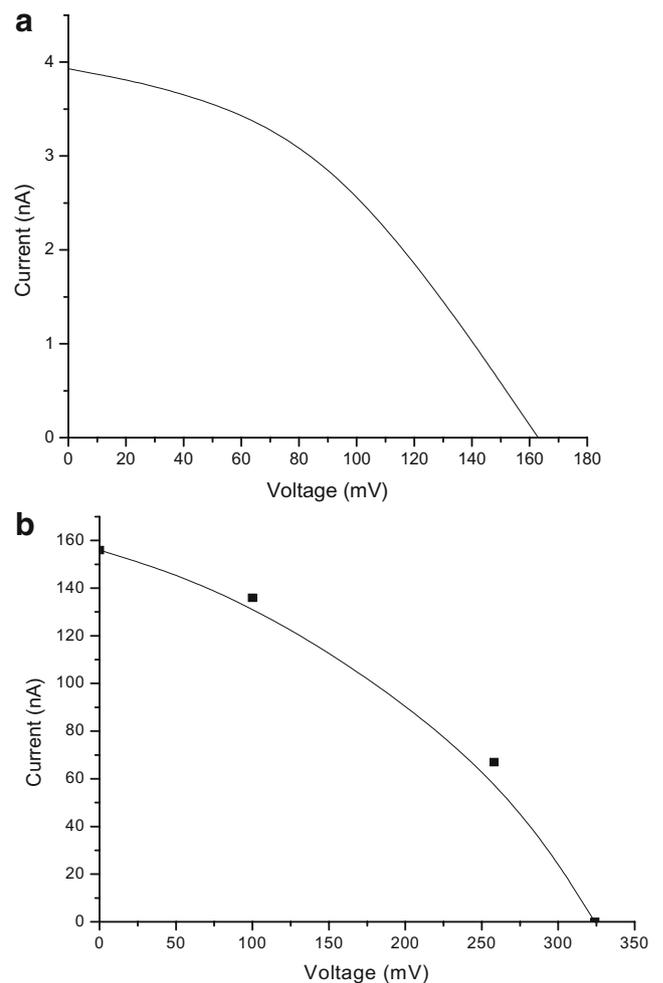


**Fig. 3** a Structure of photoelectrochemical cell. b Setup for photovoltaic measurement

England), having the absorption peak at 590 nm that has an optical band gap of the order 2.1 eV, are shown in Fig. 1a and b. Absorption spectra of two dyes [21, 22] are also shown in Fig. 2a and b.

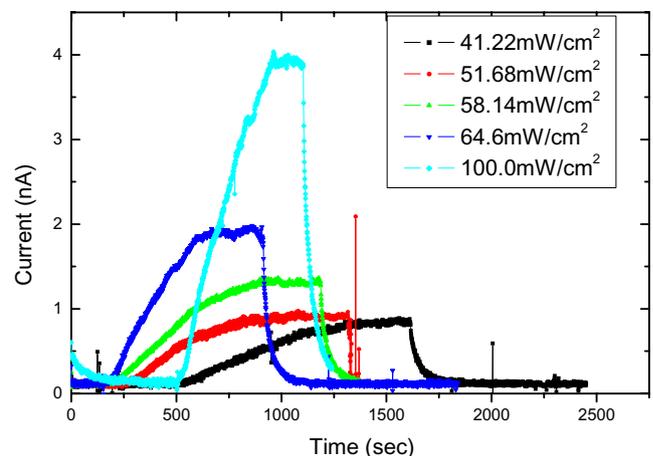
In a cleaned test tube, 1 g of PVA was mixed with 10 l of double distilled water, warmed gently, and stirred to make a transparent viscous solution of PVA (S. D. Fine Chem., Boisar; M.W. 125000). Two milligrams of methyl red (anionic dye) and 2 mg of crystal violet (cationic dye) are mixed with this solution.

A solid electrolyte was prepared in a separate cleaned beaker by mixing PEO (BDH, England; M. W. 600000)–LiClO<sub>4</sub> (Fluka, 99.5% pure)–EC (Fluka, 99.5% pure)–and PC (Fluka, 99.5% pure). The complex of PEO–LiClO<sub>4</sub> – EC–PC (30.60:3.60:19.60:46.20% by weight) were mixed, stirred, and heated around a temperature 60 °C for 4 h. This gel-like solid electrolyte is mixed with the previously prepared dye–PVA solution to form the blend. This blend is heated about a temperature 60 °C and stirred properly to mix them well for about 2 h. This viscous gel-like solution is then sandwiched between two electrodes. Thus, single layer sample is prepared. The active area of the cell was 0.16 cm<sup>2</sup>. To prepare double layer film, C<sub>60</sub> solution in dichlorobenzene layer is deposited over the single layer of viscous gel-like solution that was sandwiched between the previously said same contact electrodes. The active area of the cell was 1.08 cm<sup>2</sup>. The electrodes were cleaned in chloroform solution and dried under vacuum about 2 h before

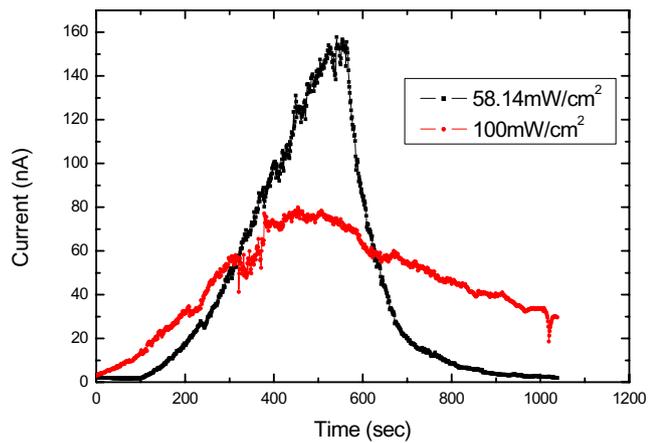


**Fig. 4** a I–V characteristics at 1 Sun incident-illumination (without C<sub>60</sub> layer). b I–V characteristics at 1 Sun incident-illumination (with C<sub>60</sub> layer)

use. The two electrical leads are taken out from the two ends of the electrodes. The complete cell is vacuum dried for about 6 h at around 60 °C before the final measurement. The structure of the cell is shown in Fig. 3a.



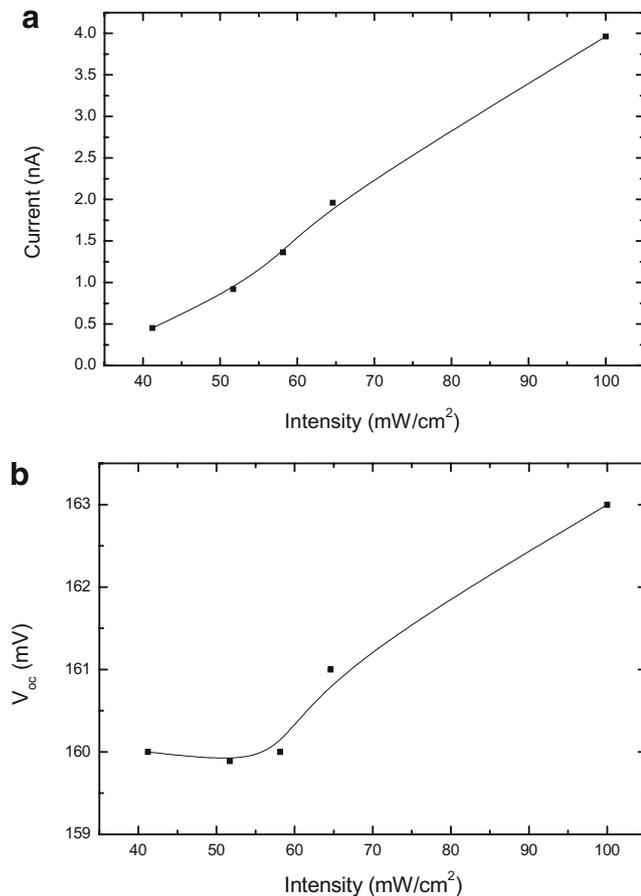
**Fig. 5** Photocurrent at different intensity of incident illumination in case of single layer structure (without C<sub>60</sub> layer)



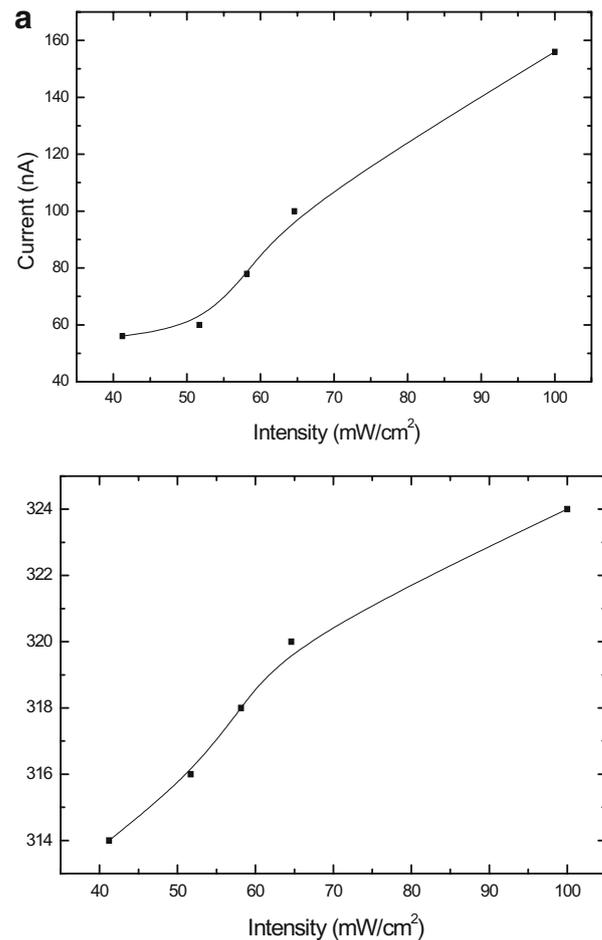
**Fig. 6** Photocurrent at different intensity of incident illumination in case of double layer structure (with C<sub>60</sub> layer)

### Measurements

For optical measurement, a tungsten lamp of 200 W is used. Light is allowed to incident on the cell. By varying the intensity of incident radiation voltage drops, hence, the photocurrent across the sensing resistance is measured. The current flowing through the device was estimated by mea-



**Fig. 7** **a** Short circuit current vs intensity curve (without C<sub>60</sub> layer). **b** Open circuit voltage vs intensity curve (without C<sub>60</sub> layer)



**Fig. 8** **a** Short circuit current vs intensity curve (with C<sub>60</sub> layer). **b** Open circuit voltage vs intensity curve (with C<sub>60</sub> layer)

suring the voltage drop (measured by Agilent data acquisition unit, Model No: 34970A) across 56 K $\Omega$  sensing resistance. The intensity is measured by a calibrated lux meter (Kyoritsu Electrical Instruments Works, Tokyo, model 5200). Photocurrent is measured by varying the intensity of light.

## Results and discussion

### Photovoltaic measurements

Setup of photovoltaic measurement is shown in Fig. 3b. From Fig. 3b, it is clear that ammeter is not required when measurement of open circuit voltage ( $V_{oc}$ ) is done. In the similar way, voltmeter does not play any role at the time of short circuit current ( $I_{sc}$ ) measurement. By changing variable resistance ( $R$ ), Fig. 4a and b are drawn. Current–voltage characteristics under 1Sun incident illumination are shown in Fig. 4a and b. Measurement of  $I_{sc}$  and  $V_{oc}$  is done under different intensity of illumination. The variation of short circuit current ( $I_{sc}$ ) with time ( $t$ ) for different intensity illumination is

shown in Figs. 5 and 6 where ITO/dye-sensitized polymer layer/Al junction is illuminated through ITO side. Furthermore, experimental evidences of this effect are presented in Figs. 7a and b, and 8a and b where the short circuit current ( $I_{sc}$ ) and the open circuit voltage ( $V_{oc}$ ) are plotted as function of intensity of incident light.

Various photovoltaic parameters such as  $V_{oc}$  and  $I_{sc}$  are obtained to be 163 mV and 3.93 nA, respectively, for 1 Sun intensity of illumination. The power conversion efficiency of each cell can be estimated by using the equation

$$\eta^{\circ}\% = \frac{I_{sc} \times V_{oc} \times FF}{\phi_0} \times 100 \quad (1)$$

where  $\phi_0$  is the incident intensity of light and FF is defined by relation

$$FF = \frac{V_m \times I_m}{V_{oc} \times I_{sc}} \quad (2)$$

Where  $V_m$  and  $I_m$  represent the voltage and current density at maximum power point, respectively. The estimated values of FF and power conversion efficiency are 0.33 and 0.00132% for 1 Sun radiation in case of single layer structure. The enhanced value of power conversion efficiency for the cell with  $C_{60}$  is 0.0153%. The photovoltaic parameters are shown in the following table.

Parameters	Cell without $C_{60}$	Cell with $C_{60}$
$V_{oc}$ (mV)	163	324
$I_{sc}$ (nA)	3.93	156
FF	0.33	0.33
$\eta$ (%)	0.00132	0.0153

Fullerene layer has also attracted a great deal of interest, which enabled to develop highly efficient optical and electrical devices. Bi-layer devices can be quite efficient in photoconversion, with the exciton dissociation occurring at the interface of the photoactive materials due to the difference of the electronaffinity values. Enhancement of photovoltaic parameters in case of bilayer/double layer in comparison to single layer reveals that, here, polymer acts as an electron donor to the second layers, whereas  $C_{60}$  plays the role of an electron acceptor.

## Conclusions

Reports on the photovoltaic property of the device made in PEC band structure are not common. In this work, photovol-

taic properties of methyl red and crystal violet dye-sensitized solid-state PEC have been described. The film was prepared by spin-coating technique. The cell without  $C_{60}$  has a fill factor of 33% and a power conversion efficiency of order 0.00132% under 1 Sun radiation, which is modified in presence of  $C_{60}$  layer. The values of fill factor and power conversion efficiency in presence of additional  $C_{60}$  layer are 33 and 0.0153%, respectively. Our results indicate the possibility of using dye-sensitized PEC devices of different architecture as solar cells.

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