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Incorporation of liquid crystalline triphenylene derivative in bulk heterojunction solar cell with molybdenum oxide as buffer layer for improved efficiency

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ABSTRACT
We report efficient bulk heterojunction solar cells fabricated by inserting a discotic triphenylene derivative into poly (3-hexylthiophene): [6, 6]-phenyl-C61-butyric acid methyl ester. A layer of molybdenum oxide was inserted between anode and active layer. Power conversion efficiency of 2.0% was achieved for these photovoltaic solar cells containing self-organised discotic liquid crystals in the active layer under one sun condition. The influence of varying the thickness of liquid crystal layer and annealing on these solar cells was also studied. Post annealing the bulk heterojunction devices with discotic liquid crystal layer of thickness 20 nm in them yielded an open circuit voltage of 0.41 V, short circuit current density of 17.0 mA cm$^{-2}$, a Fill factor of 0.35 and power conversion efficiency of 2.5%.

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KEYWORDS
Discotic liquid crystal; bulk heterojunction; optical band gap; annealing; current density

1. Introduction
Discotic liquid crystals (DLCs) possess exceptional properties that can be effectively exploited for use in organic photovoltaic (OPV) devices. DLCs have the propensity to self-assemble over large areas into well-ordered columnar structures in the form of uniform, thin films because of their fluidity \cite{1}. Columnar structures are formed by disc-shaped molecules made of bulky aromatic cores encircled with flexible aliphatic chains which can absorb radiations from the entire solar spectrum \cite{2}. These molecules stack one on top of the other by means of good $\pi$-orbital overlap between the neighbouring cores \cite{3,4}. The strong $\pi-\pi$ interactions between the cores allow the charge carriers to move easily from molecule to molecule over large distances along a column. Thus, the columns formed by DLCs in their mesophases provide large diffusion length and high charge carrier mobilities which are of paramount importance while determining the efficiencies of OPV cells \cite{5}.

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The operation of OPV devices includes the absorption of photons, creation of electron hole pairs called excitons, dissociation of excitons into holes and electrons and ultimately, the collection of charge carriers at the respective electrodes [6–8]. Bulk heterojunction (BHJ) solar cells give best power conversion efficiencies (PCE) as the intermixing of the p-type donor and n-type acceptor semiconductors maximises the interfacial area for charge separation [9]. But the performance of these OPVs is limited by numerous factors such as aligning the donor and acceptor semiconductors is difficult to achieve. They are not thermodynamically stable. Also, the exciton diffusion length in polymer-based BHJ solar cells is in the range of 10 nm [10]. Another prerequisite of organic materials for their beneficial use in solar cells is high charge carrier mobility to ensure uninterrupted transport of charge carriers to the respective electrodes. Therefore, DLCs which fulfil the above criteria are promising candidates for BHJ solar cell applications. Gregg et al. [11] were the first to use a liquid crystal porphyrin in symmetrical solar cells in 1990. The authors further averred that space charge layer is not compulsory to realise photovoltaic effect and under zero interfacial voltage, hole injection is most likely to be twenty times more than electron injection [11]. He et al. [12] reported a high open circuit voltage of 0.89 V and PCE of 4.8% in OPV devices using a discotic thienoazacorone acting as donor material. Schmidt-Mende et al. [13] fabricated solar cells by blending a perylene derivative and a room temperature DLC, hexaphenyl-substituted hexabenzocoronene and achieved a power conversion efficiency of 2%. Also, it has been demonstrated that BHJ solar cells made from liquid crystal conjugated polymers show favourable performances upon annealing the mesophase due to increased structural order and crystallinity [14–16].

In this study, we investigate the photovoltaic effect on BHJ solar cells fabricated by using triphenylene compound with six β-side chains (i.e. 2,3,6,7,10,11-hexabutyloxytriphenylene (HAT4)) layer of varying thicknesses in it. HAT4 is a discotic liquid crystalline material showing a plastic columnar hexagonal phase. This DLC is soluble in common non-polar solvents and is thermally stable in its mesophase [17]. Molybdenum oxide (MoO3) has been used as a buffer layer between indium tin oxide (ITO) and active layer instead of the conventionally used poly (3,4 ethylenedioxythiophene)-poly (styrenesulfonate) (PEDOT:PSS) since it can enhance device efficiency and can provide stability to solar cells.

2. Experimental techniques

2.1. Synthesis of discotic liquid crystal and characterisation

The structure of HAT4 is shown in Figure 1b. The detailed procedure for the synthesis of the discotic liquid crystal, HAT4 has been reported elsewhere [18]. Differential scanning calorimetry (NETZSCH DSC – 200-F3-Maia) was used to determine melting and clearing temperatures and their respective enthalpies. UV-visible spectroscopy studies were performed using a spectrophotometer (Shimadzu – model UV-1800) in the wavelength range of 190–900 nm. Polarising optical microscopy (POM, polarising optical microscope) equipped with an Instec MK1000 heating stage was used to take snapshots of the DLC at different temperatures during cooling from 10°C above the

![Figure 1.](image-url) (colour online) (a) Schematic device configuration of bulk heterojunction solar cells with DLC layer (b) molecular structure of HAT4.
isotropic temperature. Two flat glass plates coated with transparent ITO kept on top of other were used for these studies. Mylar spacers of 10 µm thickness were used to maintain gap between the glass plates. In order to avoid use of adhesive, these parallel plate capacitor type cells were clamped in a sample holder.

2.2. Solar cell fabrication and measurements

All of the devices were fabricated with a structure of glass/ITO/MoO$_3$/HAT4/P3HT:PCBM/Al by changing the thickness of HAT4 layer in them. ITO-coated glass substrates with a sheet resistance of 18 Ω/□ were used as the anode. The glass substrates were kept in detergent solution and ultrasonicated for 10 min. followed by rinsing in deionised water. Subsequently, they were boiled in acetone, trichloroethylene and propanol. They were dried at each step for 10 min at a temperature of 90°C. Thereafter, a thin film of MoO$_3$ (procured from Sigma Aldrich, USA) was deposited onto the pre-cleaned plasma-treated ITO-coated glass substrates by vacuum deposition technique. The plasma exposure of the substrates improves the work function of ITO and its wettability. HAT4 films of varying thicknesses were deposited by vacuum thermal evaporation at pressure of 10$^{-6}$ Torr on top of these substrates. poly (3-Hexylthiophene) (P3HT) and [6, 6]-phenyl-C61-butyric acid methyl ester (PCBM) from Sigma Aldrich were used without purification. Blend of P3HT: PCBM achieved with a weight ratio of 1: 1 in 10 mg ml$^{-1}$ chlorobenzene solution was deposited by means of spin coater unit. Magnetic stirrer was used to homogenise the solutions for 24°h. Top electrodes of aluminium having thickness of 100 nm were applied through a shadow mask by vacuum evaporation. Prior to testing, the devices were annealed for 15 min at 120 °C in ambient atmosphere. The morphology of films was studied by the help of atomic force microscopy (AFM) in tapping mode. Current density–voltage (J–V) characteristics of the fabricated devices were measured using a Keithley 2400 source meter unit interfaced with a computer under illumination of 100 mW cm$^{-2}$ intensity.

3. Results and discussion

Figure 1a depicts a schematic representation of BHJ solar cells based on the triphenylene compound, HAT4. MoO$_3$ has been used as a buffer layer between the anode and the active layer. A pivotal role is played by the oxide layer in providing long-term stability to solar cells and preventing unnecessary chemical reaction between the anode and the active layer [19]. HAT4 is known to act as electron donor in many liquid crystal nanocomposites because it possesses an electron-rich aromatic core. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of P3HT is higher than that of PCBM, so P3HT and PCBM act as donor and acceptor respectively in the fabricated devices.

The operation of photovoltaic devices depends on the position of energy levels of its assorted components. Energy levels of the organic materials used in the devices are presented in Figure 2 which has been compiled from various reported results [20–22]. UV-visible absorption spectra for HAT4 can be seen in Figure 3. The optical band gap of pure HAT4 was calculated from the optical absorbance curve. The optical band gap ($E_g$) for organic materials corresponding

![Figure 2. The energy level diagram for bulk heterojunction solar cells.](image)

![Figure 3. (colour online) Optical absorbance spectra for pure HAT4](image)
to definite transition between HOMO and LUMO energy levels and absorption coefficient ($\alpha$) is governed by the following equation [23]:

$$\alpha E = A(E - E_g)^n$$  \hspace{1cm} (1)

where, $E = h\nu$ is energy of incident photon and value of $n$ determines the nature of transition. $n$ can take values of 1/2, 2, 3/2, 3 which correspond to allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. The value of optical band gap is estimated by plotting graph between $(\alpha E)^{1/n}$ and $E$ with its linear region extrapolated to $\alpha E = 0$. The band gap for HAT4 is calculated to be ~4 eV. The LUMO energy levels of HAT4 and P3HT are higher than PCBM which generates sufficient driving force for separation of charge carriers after photo excitation.

The performance of the BHJ solar cells is determined by measuring its current–voltage ($J$–$V$) characteristics in dark and under sun light illumination. $J$–$V$ characteristics of ITO/MoO$_3$/HAT4:PCBM:P3HT/Al devices with HAT4 layer of different thicknesses under dark are shown in Figure 4. When forward bias is applied to the devices, large current flows through them as the charge carriers gain sufficient energy to overcome the internal barrier potential. However, the application of reverse bias leads to increase in barrier potential by the external field, due to which only small current flows in the devices [24]. So, under dark condition, all devices show the behaviour of a rectifier. $J$–$V$ curves of this type follow the given equation [24]:

$$J = J_0 \left( \exp \left( \frac{qV}{mkT} \right) - 1 \right)$$  \hspace{1cm} (2)

where, the symbols $J_0$, $q$, $V$, $m$, $k$ and $T$ represent the reverse saturation current density, electronic charge, applied voltage, diode quality factor, Boltzmann’s constant and temperature, respectively. All the devices designed with HAT4 layer of varying thicknesses obey the above equation.

Figure 5 shows the $J$–$V$ characteristics of the devices under 100 mW/cm$^2$ white light illumination conditions showing photovoltaic properties. The illuminated current is the combination of dark current as well as photocurrent. Therefore, the current under illumination can be obtained from equation [24]:

$$J = J_p - \left( J_0 \left( \exp \left( \frac{qV}{mkT} \right) - 1 \right) \right) \hspace{1cm} (3)$$

$J_p$ is the current which flows under illumination. Illuminating the devices leads to the absorption of photon which generates the excitons (electron-hole pair). Due to the internal field that is present at the junctions, the excitons get separated into charge carriers and current flows in the devices. The cell performance parameters such as short circuit current ($I_{sc}$), open circuit voltage ($V_{OC}$), fill factor (FF) and PCE calculated from these $J$–$V$ characteristics have been accumulated in Table 1. FF is the measure of the power that can be extracted from a solar cell and is defined as the ratio between the maximum power that the solar cell can deliver and the maximum power that it could deliver under ideal lossless conditions. Ideally, the value of FF should be unity, but because of losses such as transport and recombination of charge carriers, its value is always less than unity for organic photovoltaic devices. For the above fabricated devices reported here, FF lies between 0.2 and 0.4. The device without HAT4 layer showed poor performance.
yielded a $J_{sc}$ of 7.43 mA cm$^{-2}$, a $V_{oc}$ of 0.43 V, a calculated fill factor of 0.29 and a PCE of 0.93%. However, PCE improved by 63% after addition of HAT4 layer in it. It can be seen that $J_{sc}$ also improved significantly from 7.4 mA cm$^{-2}$ to 11.6 mA cm$^{-2}$ in DLC-incorporated solar cells. Although the factors affecting $J_{sc}$ have not been recognised, the low mobility of the charge carriers in the devices, the morphology of the active layer and the interface of the device restrict the short circuit current and PCE of polymer solar cells [25]. The enhancement in $J_{sc}$ can be ascribed to the increased charge separation and decrease in charge recombination in the photoactive film, enabled by HAT4 layer in these devices. These results arise from the more uniform mixing and increase in the intermolecular interactions between the liquid crystalline chains and polymers.

Photovoltaic parameters were also studied by varying the thickness of HAT4 layer in the devices. The value of PCE was 0.96%, 1.60%, 1.74%, 2.00%, 0.69%, 0.68% and 0.27% when thickness of DLC layer was 1, 5, 10, 20, 30, 40 and 50 nm, respectively. The $J_{sc}$ and PCE of measured devices show an overall increase with increasing the thickness of HAT4 layer and reach a maximum of 11.60 mA cm$^{-2}$ and 2% when thickness was kept at 20 nm (see Figure 6). As the thickness is increased beyond 20 nm, the values of $J_{sc}$ and efficiency drop significantly. The reason for this effect can be the creation of traps on increasing thickness. The increased thickness leads to reduction in charge carrier lifetime and enhanced recombination of carriers by the traps which are introduced in the active layer [26]. Also, device resistance is increased by use of thick active layer [27].

Effect of annealing on the photovoltaic parameters of the devices was studied as well. The annealing process controls the morphology of the active layer and the device performance is largely influenced by it. To know about the thermotropic behaviour of HAT4, the thermal properties were investigated by means of DSC. Figure 7 represents the DSC curves for HAT4 taken while heating and cooling at scan rate of 5°C min$^{-1}$. They show two discrete peaks signifying crystal-colum- 

<table>
<thead>
<tr>
<th>Thickness of HAT4 layer</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
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<tbody>
<tr>
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Table 1. Photovoltaic parameters, open circuit voltage ($V_{oc}$) in Volt, short circuit current ($J_{sc}$) in mA cm$^{-2}$, fill factor (FF) in % and power conversion efficiency (PCE) in % for devices without HAT4 layer and with HAT4 layer (thickness in nm) in it taken before annealing.
which columns are aligned parallel to the substrates called as planar alignment and in the other columns get aligned perpendicular to the substrates known as homeotropic alignment [28,29]. Homeotropic alignment of columns is required for photovoltaic operation to ensure transport of charges from active layer to electrodes in direction perpendicular to the glass plates. HAT4 molecules self-arrange under homeotropic orientation, that is, columns are perpendicular to the electrodes with the disc-shaped molecules lying flat on the surface of substrate on slow cooling at the rate of 0.1°C min⁻¹ from their isotropic melt confined between substrates [30]. This orientation happens to be the minimum energy position also. Figures 8 and 9 represent the J–V characteristics recorded under dark and illumination for the annealed devices with HAT4 layer of varying thickness. The devices showed enhanced performance post annealing. A marked difference was observed in the increase of Jₓc and PCE on comparing the J–V curves of annealed devices with that of the unannealed devices. The device parameters for these cells are summarised in Table 2. The devices without HAT4 layer in them were not affected by thermal annealing. The Jₓc and efficiency of the devices with HAT4 layer increased to 17.0 mA cm⁻² and 2.5% respectively after annealing. Jₓc is directly proportional to charge carrier mobility and is defined by the given equation [31]

\[
J_{sc} = ne\mu E
\]

where, n is the charge carrier density, e is elementary charge, μ is mobility and E is electric field. Incorporation of HAT4 layer in the devices leads to high charge carrier mobility due to which increase in Jₓc is obtained. The degree of order present within columns of disc-shaped molecules and overlap of π orbitals determines the mobility [32]. High charge carrier mobilities prevent trapping of excitons and efficient separation of charges takes place. Also, HAT4 flaunts plastic columnar hexagonal phase which is ordered phase [33]. The enhanced performance implies that HAT4 favours the whole active layer to form well-ordered morphology for better charge transport, and annealing from the liquid crystalline mesophases can reduce the density of defects at the interface. The organisation of the discs after undergoing thermal treatment strengthens their crystallinity. Hirota et al. [34] engineered spin-coated photovoltaic devices containing poly [2-methoxy-5-(2’-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and discotic 1,7,13-heptanoylecacyclone which showed a relatively high open circuit voltage of 1.3 V and indicated an improvement in charge transport after thermal annealing. Han et al. [35] achieved enhanced efficiency of 1.3% and

<table>
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<th>Vₒc (V)</th>
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<th>PCE (%)</th>
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<td>1.51</td>
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Table 2. Photovoltaic performance parameter, open circuit voltage (Vₒc) in Volt, short circuit current (Jₓc) in mA cm⁻², fill factor (FF) in % and power conversion efficiency (PCE) in % for devices without HAT4 layer and with HAT4 layer (thickness in nm) in it taken after annealing.
1.2% in thermally annealed films of diketopyrrolopyrrole-based liquid crystalline conjugated donor acceptor copolymers. It has been reported that by utilising liquid crystalline rod-coil block copolymers as compatibilizers in P3HT:PCBM blends, the photovoltaic performance of P3HT:PCBM solar cells could be significantly improved at the optimal concentration of liquid crystalline rod-coil block copolymers, especially after annealing from the mesophases \cite{36}. An increase in the surface ordering of composites for solar cells based on P3HT, PCBM and two different chiral photosensitive liquid crystal (LC) materials after annealing was reported by Iwan et al. and Bubnov et al. \cite{37–39}.

The morphological properties of surface of HAT4 film of varying thicknesses has been investigated by AFM technique. Figures 10 and 11 show the topographic surface images and three-dimensional view for HAT4 layer with thickness of 10 and 20 nm, respectively. The surface morphology is quite smooth and homogeneous of HAT4 film of thickness 20 nm as compared to image of HAT4 film of thickness 10 nm. When thickness of HAT4 film is 20 nm, the columns formed by discotic molecules get arranged properly providing favourable channels for charge carrier transportation to respective electrodes \cite{40}. This result is in conformation with J–V characteristics in which value of PCE is maximum when the thickness of HAT4 layer is 20 nm.

4. Conclusion

BHJ photovoltaic cells based on self-assembling discotic liquid crystalline triphenylene derivative have been fabricated with MoO3 as a buffer layer. The performance of devices with inserted HAT4 layer shows that DLCs can be effectively used for achieving efficient photovoltaic cells. DLCs provide favourable pathways for transportation of charge carriers to their respective electrodes since they can act as one-dimensional conductors. An increase in the performance of the devices is achieved also because defects are removed and morphology of active layer is optimised by thermal annealing of the devices within the temperature range of mesophase. These results confirm that DLCs provides an opportunity to develop thermally stable and highly ordered molecular systems in the field of photovoltaics.

Disclosure statement

No potential conflict of interest was reported by the authors.
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