Ionically Gated Small Molecule OPV: Controlled n-doping of Thick Fullerene acceptor layers

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Abstract

We demonstrate the controlled n-doping in small molecule organic photovoltaic (OPV) systems by ionic gating of multi-wall carbon nanotube (MWCNT) coated fullerenes: $C_{60}$ and $C_{70}$. Such electric double layer charging (EDLC) doping, achieved by ionic liquid (IL) charging, allows tuning the electronic concentration in the acceptor layers, increasing it by orders of magnitude. This leads to decreasing both the series and shunt resistances of OPV and allows to use thick (up to 200 nm) electron transport layers, increasing the durability and stability of OPV. Two stages of OPV enhancement are described, upon increase of gating bias: at small (or even zero) $V_g$ the interface between
porous transparent MWCNT charge collector with fullerene is improved, becoming an ohmic contact. This changes the S-shaped I-V curve and improves the electrons collection by a MWCNT turning it into a good cathode. The effect further enhances at higher $V_g$ due to raising of Fermi level and lowering of MWCNT work function. At next qualitative stage, the acceptor layer becomes n-doped by electron injection from MWCNT and ions penetration into fullerene. At this step the internal built-in field is created within OPV, that helps exciton dissociation and charge separation/transport, increasing further the $I_{sc}$ and the $FF$ (Filling factor). Overall power conversion efficiency (PCE) increases nearly 50 times in classical CuPc/fullerene OPV with bulk heterojunction photoactive layer and MWCNT cathode. Ionic gating of MWCNT-fullerene part of OPV opens a new way to tune the properties of organic devices, based on controllable and reversible doping and modulation of work function.

**Keywords**

Carbon nanotubes, Electrodes, Small molecules, Organic solar cells, Fullerene, Doping, Ultracapacitors

**Introduction**

Organic photovoltaics is one of the competing technologies in the modern renewable energy sector, which is capable to partially meet the needs of power generation due to many advantages such as low cost, extreme flexibility, lightweight and large-area manufacturing. Since the pioneering work by Ching W. Tang on two-layer OPV cell based on molecular donor-acceptor structure of CuPc and perylene tetracarboxylic derivative with a PCE of about 1%, the significant progress has been achieved in understanding and improvement of OPV systems, leading to a PCE of over 11% in single-junction and over 13% in tandem OPV small molecule-based devices that are not so far from the commercialization threshold.
A rather quick increase in performance of OPV solar cells has happened mainly due to the synthesis of better organic materials with higher charge mobility. However, it is not the only way, and further improvement is still possible since those OPV cells are usually undoped bulk heterojunction (BHJ) type structures. If the doping of transport layers can be easily achieved then additional enhancement of efficiency will be a straightforward success. It is well known that p-i-n OPV solar cells have better performance and are more stable due to the thicker p-doped hole transport layer (HTL) and the n-doped electron transport layer (ETL) with low series resistance. In a series of papers, p- and n-type electronic doping of organic donor (D) and acceptor (A) transport layers has been shown to increase the performance of OPV cells, and 8-10% efficiency has been achieved in tandems, demonstrating great promise of p-i-n organic structures.

One of the outcomes of creating true p-i-n structures as opposed to intrinsic, undoped D-A structures (which are commonly and mistakenly called sometimes as p-n diodes), is the advantage of using thick transport layers with very low series resistances. So C₆₀ layers of n-doped A(n) ETL as thick as 100 nm has been used, as opposed to usual thickness of intrinsic A(i) layer of 7-10 nm. Such thicker layers allow achieving more durable OPV structures without pin-holes. We do not discuss here the obvious advantages of p-i-n structures, such as ohmic contacts with electrodes (and non-sensitivity to work function of an electrode), better charge separation by built-in electric fields, and many others (well described, e.g., in reviews of Karl Leo team).

Indeed, truly doped p-i-n geometry improves the separation of positive and negative charges by built-in potentials, and it also decreases series resistance, enhancing PCE. The most significant progress here is obtained by charge-transfer (CT) type doping the donor layers (e.g. of phthalocyanine by active acceptor molecules, such as F₄–TCNQ). Such CT-doping as opposed to substitutional doping (as P and B atoms substitution in Si crystal and other inorganic semiconductors) is usually achieved by intercalation of strong CT dopant between molecules of a host: so most recently and successfully obtained by co-evaporation
of strong organic molecular donors (such as acrylic orange, or usual Li atoms) into C$_{60}$ layers.$^{15}$ However, such CT doping is usually done in low molecular OPV systems using air sensitive dopants in a high vacuum process,$^{8,10,11}$ which is very sophisticated and expensive, and cannot be used for liquid-based air processing of small molecule BHJs OPV cells, while the recent progress with PCE of $\sim$ 10% is namely due to solution processing.

Doping with the optimum concentration of electrons or holes can modify the physical properties of both A and D layers in organic electronic devices, particularly in OPV and OLED. Therefore, improved ways to achieve carrier doping have been pursued extensively in organic electronics arena, with metal-intercalation, (as mentioned above Li-intercalation into C$_{60}$ films) is one of the most important techniques for electron doping of organic/inorganic solids, and has produced not only efficient p-i-n OPV, but also C$_{60}$ and FeSe superconductors from insulators and metallic solids.$^{16}$ The most successful examples here are metal-intercalated graphite and C$_{60}$ superconductors. Such metal or organic molecule (TCNQ, etc.) intercalation has been performed using not only vacuum co-evaporation but also by liquid solvent techniques. Strong donor (e.g., Li, Na or acrylic orange) intercalation can donate electrons to acceptor ETL layer, which shifts the Fermi level upward.

Recently, the electric-double-layer charging (EDLC) has attracted significant attention as a new way to control the carrier density at the interface of nanoscale materials, particularly at the contacts with carbon nanotubes (CNTs)$^{17}$ and graphene$^{18}$ which can be achieved reversibly and with no change of chemical composition or structure. Various novel physical properties such as superconductivity,$^{19-21}$ metal-insulator$^{22}$ and ferromagnetism$^{23}$ have been shown. We have demonstrated first that tunable polymeric OPV can be created using IL for gating type charging by a formation of the EDLC capacitive doping of single-wall carbon nanotube (SWCNT) and MWCNT.$^{24,25}$

The cathode material is another factor that hinders the performance improvement of OPV cells mostly due to its low stability in air conditions and special processing requirements. Therefore, Al or Ag electrodes are less attractive for use in OPV cells. Air-stable CNTs
have successfully demonstrated their ability to function as a transparent electrode in small molecule OPV cell with doped HTL and ETL layers. However, such n-i-p OPV device with n-doped C\textsubscript{60} and CNT anode on the top of p-type HTL have a certain drawback since it was prepared in high vacuum by co-evaporation doping of C\textsubscript{60} with a very expensive dopant. This inspired us to develop a new architecture deprived of this shortcoming. Here, we propose another structure that is more advantageous since n-doping of both MWCNTs and fullerene can be done in ambient conditions with no need for any additional high-priced processing. MWCNTs have initially a value of sheet resistance $R_{\text{sheet}}$ exceeding 1000 $\Omega$/sq in the undoped as-synthesized state that is very high for PV applications. The work function of CNTs in our OPV cell can be substantially modified by EDLC under IL gating, turning them into a good cathode. In other words, the Fermi level of MWCNTs can be raised up by n-type doping, thereby allowing better electron collection from the active layer of OPV cell, and a value of $R_{\text{sheet}}$ can be decreased to the acceptable level below 100 $\Omega$/sq. In an EDLC ionic gating method, the carriers can first accumulate around the extended interface of highly porous nanomaterial, such as CNT, and their concentration and work function can be controlled by an electric field of the gate $V_g$. Such simple reversible and tunable EDLC-doping has never been previously used in small molecule OPV cells.

So motivation of our present paper is to create a small molecule OPV device in which n-doping can be easily achieved in a system of porous CNT electrode coated on top of fullerene film ETL of a most simple two-layer OPV: CuPc/fullerene with methods of reversible ionic EDLC. This requires new architecture, which combines IL supercapacitor, connected in parallel with OPV as we introduced earlier for a polymeric OPV with IL, and demonstrated its advantages in tandems. In this paper, we apply the gating in IL to classical small molecule OPV with DEME–BF\textsubscript{4} IL and study the dynamics of this ionically gated system of MWCNT@Fullerene (i.e. cathode@ETL) to understand how it accumulates electrons, and how the ions move first in MWCNT network and then into and through fullerene molecular ETL layer of different
thicknesses. We show here that this process differs significantly from the case of polymeric OPV, studied in our earlier paper, since in a thick molecular fullerene film (with molecules bonded by Van der Waals forces) there are clear three stages of charging and n-doping of separately MWCNT and fullerene subsystems.

**Experimental**

Small molecule OPV cell was prepared in the multi-source resistive glove box integrated high-vacuum system (Angstrom Engineering Inc., Canada) by the sequential thermal evaporation onto UV-ozone threatened, patterned ITO-glass substrates of the following layers: a 7 nm thick copper(II) phthalocyanine (from H.W. Sanders Corp) HTL, a 60 nm thick co-evaporated with a smooth gradient CuPc:fullerene mixed D:A layer and top fullerene layer of a variable thickness. The following fullerene materials were used: C$_{60}$ or C$_{70}$ (both >98% from Nano-C) for different devices. The base pressure of the chamber was kept around 10$^{-8}$ mbar during the evaporation.

![Image of OPV device](image1)

**Figure 1:** View of OPV device with laminated semi-transparent MWCNT cathode and MWCNT counter-electrode soaked by ionic liquid (left) and measurement setup and electrical connection scheme for determination of solar cell parameters when gate voltage $V_g$ applied (right).

MWCNT forest was produced by a chemical vapor deposition (CVD) process. Our OPV devices contain three electrodes: an anode of the solar cell (ITO under CuPc), a cathode
(first MWCNT sheet on top of fullerene ETL) and a counter-electrode (second MWCNT sheet). Both MWCNT cathode and another MWCNT electrode named "counter-electrode" or gate were deposited by manual dry lamination on the top of organic multilayer structure outside the glovebox in ambient conditions. After that, the deposited MWCNTs were immersed in liquid hydrofluoroether (HFE) solvent for several seconds to condense tube to tube interconnects and therefore improve conductivity and stability of the electrodes. Contacts for cathode, counter-electrode, and ITO-anode were created using silver paint. A small amount of ionic liquid, $N,N$-Diethyl-$N$-methyl-$N$-(2-methoxyethyl) ammonium tetrafluoroborate, $\text{DEME}^-\text{BF}_4$ (Kanto Chemical Co. Inc.), was dropped on top of both MWCNT electrodes. A thin transparent glass cover-slip was placed over the ionic liquid. A general view of one fabricated OPV device is shown on the left panel of Fig. 1.

Figure 2: Side view of the OPV-CNT-IL test cell. Light shines through the bottom transparent conductive oxide cathode (ITO) and into the CuPc/fullerene mixed active layer. Ions can EDLC charge on a surface of CNT and move further through the porous CNT into the small molecule fullerene matrix of OPV, doping adjacent CNT cathode layers, which are tested for different thicknesses up to 200 nm.

OPV devices were characterized with an AM 1.5G solar simulator calibrated to one sun (100 $mW/cm^2$), and two LabVIEW controlled Keithley 2400 source measure units (SMU) in a nitrogen glove box. One of these SMUs was used to apply a gate voltage ($V_g$) by connecting
Figure 3: I-V curves of the OPV solar cell with a 5 nm-thick C$_{60}$ ETL at different values of gate voltage under illumination (a) and the extracted parameter for the same solar cell as a function of gate voltage (b). OPV device shows its best performance at $V_g = 0.85$ V.

counter-electrode with MWCNT cathode while the second SMU measured I-V parameters of OPV cells through connection to the anode and cathode of OPV part (see right panel of Fig. 1). Application of a bias $V_g$ between the MWCNT cathode and MWCNT counter-electrode would thus produce super-capacitive EDLC while measurements under of $I$, and $V$ between the ITO anode and MWCNT cathode would result in the photovoltaic I-V curve from which we get $V_{oc}$ and $I_{sc}$ response. Such EDLC creates an asymmetry between the anode (ITO) and cathode by the decreased work function of the MWCNTs forming built-in electric field that allows better charge collection.

**Results and discussions**

Here we show the I-V measurement results of several OPV devices differing by fullerene’s type (C$_{60}$ or C$_{70}$) and ETL thicknesses (from 5 nm to 200 nm). We have found that the solar cell’s I-V parameters improved significantly even without any bias voltage between the counter-electrode and cathode just after applying the IL to the MWCNTs. In series of Figs. 3, 4, 6 we demonstrate that I-V curves corresponding to $V_g = 0$ V after IL application
Figure 4: (a) Cross-section schematics of the OPV device with top C\textsubscript{60} ETL and laminated MWCNT cathode soaked in DEME−BF\textsubscript{4} IL. (b-d) IV curves at different values of gate voltage under illumination for 40, 100 and 200 nm thick C\textsubscript{60} ETL.

experience a notable shift to higher absolute values of $I_{sc}$ leading to increase in PCE of the OPV cell. $I_{sc}$ increases due to better charge separation by i-n junctions formed in fullerene by EDLC doping.

To see the $V_g$ gate bias voltage dependence of the photovoltaic effect, we applied different bias voltages between the counter-electrode and the MWCNT@C60 cathode on ETL part of OPV. In this experiment, we used the charging time of 2 mins. After applying a bias voltage from 0 to 3V, the dependence of all three parameters of OPV, namely the $I_{sc}$, $V_{oc}$ and $FF$ were measured. Extracted OPV parameters for two specific devices are summarized
in Tables 1 and 2. Figs. 3, 4, 6 shows the bias voltage dependence of the I-V curves at step-by-step increased $V_g$ for different thicknesses of fullerene layer.
Table 1: Output parameters for the ionically gated OPV cell with 40 nm-thick C$_{60}$ ETL.

| $V_{\text{gate}}$ (V) | $I_{\text{SC}}$ (mA/cm$^2$) | $V_{\text{oc}}$ (V) | $FF$ | PCE (%) | $R_s$ (Ω $\cdot$ cm$^2$) | $R_{sh}$ (Ω $\cdot$ cm$^2$) |
|---------------------|-----------------------------|---------------------|------|---------|--------------------------|--------------------------|
| dry                 | 0.154                       | 0.276               | 0.145| 0.0062  | ...                      | ...                      |
| 0                   | 0.479                       | 0.240               | 0.135| 0.016   | ...                      | ...                      |
| 0.25                | 1.193                       | 0.321               | 0.159| 0.061   | 1222.52                  | 178.74                   |
| 0.5                 | 1.805                       | 0.404               | 0.186| 0.136   | 690.49                   | 192.18                   |
| 0.75                | 2.259                       | 0.442               | 0.234| 0.234   | 437.81                   | 250.73                   |
| 1                   | 2.558                       | 0.449               | 0.290| 0.333   | 207.37                   | 300.64                   |
| 1.25                | 2.704                       | 0.449               | 0.328| 0.398   | 115.53                   | 326.04                   |
| 1.5                 | 2.784                       | 0.442               | 0.354| 0.436   | 93.89                    | 341.14                   |
| 1.75                | 2.881                       | 0.442               | 0.386| 0.492   | 72.13                    | 351.88                   |
| 2                   | **2.959**                   | **0.434**           | **0.400**| **0.514**| **62.88**              | **469.13**               |
| 2.25                | 3.007                       | 0.411               | 0.389| 0.481   | 58.22                    | 357.95                   |
| 2.5                 | 2.990                       | 0.389               | 0.365| 0.425   | 58.08                    | 289.08                   |
| 3                   | 1.602                       | 0.080               | 0.230| 0.030   | 53.42                    | 48.26                    |

between MWCNT and n-doped fullerene and also due to the increase in conductivity of MWCNT electrode and doped fullerene. Table I shows almost 20 times increased $I_{\text{sc}}$, nearly twice increased $V_{\text{oc}}$ and $FF$ and sufficiently increased PCE from the value less than 0.01% to 0.514% (more than 50 times).

Lower $I_{\text{sc}}$ of our OPV device with MWCNTs comparing to the conventional non-transparent cathodes is caused by the reduced optical absorption in the bulk heterojunction since thick metals reflect more unabsorbed light back than semi-transparent CNTs that was already investigated in details by optical simulations for different transport layer thicknesses in our previous work.26 Another reason for the overall low PCE is the fact that these devices are unoptimized. Since this is a new device one should optimize the OPV thickness and IL volume. We believe that increasing OPV thickness and decreasing IL volume will increase PCE significantly. Small deviations from the trend can be interpreted as variations caused by manual processing and non-uniformity of materials used from different batches.

Let us consider the physical and photo-electrochemical processes in this IL-OPV device in more detail. In small molecule OPV structure, the photon absorbed in CuPc (D-part) of BHJ creates an exciton, which dissociates at fullerene interface (acceptor part) by electron injection to LUMO of fullerene. This electron is further collected via the i-n build-in field
Figure 6: (a) Cross-section schematics of the OPV device with top C$_{70}$ ETL and laminated MWCNT cathode soaked in DEME–BF$_4$ IL. (b-d) IV curves at different values of gate voltage under illumination for 50, 100 and 140 nm thick C$_{70}$ ETL.

fullerene(i)-fullerene(n) at the porous MWCNT network cathode of OPV. Positive charges in the CuPc molecules are collected by ITO anode which charges it positively, generating initial $V_{oc}$. Positively charged ions from ionic chamber redistribute around the negatively charged MWCNT cathode, creating EDLC on each nanotube or nanotube bundle and stabilizing the desired n-doping of the cathode. This doping raises the Fermi level in MWCNT cathode. Moreover, some ions distribute further between the molecules of fullerene films which stabilizes the photogenerated electrons, creating a small n-doped layer around CNT and forming a desired ohmic contact at the interface with the MWCNT cathode. Namely
Figure 7: Extracted parameter for the OPV solar cell with C$_{70}$ ETL of different thickness as a function of gate voltage.

Table 2: Output parameters for the ionically gated OPV cell with 50 nm-thick C$_{70}$ ETL.

| $V_{\text{gate}}$(V) | $I_{\text{SC}}$(mA/cm$^2$) | $C_{\text{oc}}$(V) | F$\text{F}$ | PCE(%) | $R_s$(Ω·cm$^2$) | $R_{sh}$(Ω·cm$^2$) |
|----------------------|-----------------------------|-------------------|-----------|--------|----------------|----------------|
| dry                  | 0.733                       | 0.254             | 0.199     | 0.037  | ...            | ...            |
| 0                    | 1.614                       | 0.344             | 0.184     | 0.102  | ...            | ...            |
| 0.25                 | 2.071                       | 0.420             | 0.217     | 0.188  | 1197.70        | 214.11         |
| 0.5                  | 2.467                       | 0.457             | 0.267     | 0.301  | 252.06         | 311.71         |
| 0.75                 | 2.653                       | 0.457             | 0.310     | 0.376  | 125.41         | 304.59         |
| 1                    | 2.708                       | 0.457             | 0.317     | 0.392  | 111.18         | 300.24         |
| 1.25                 | 2.764                       | 0.457             | 0.323     | 0.408  | 107.65         | 300.40         |
| 1.5                  | 2.783                       | 0.457             | 0.324     | 0.412  | 105.60         | 288.81         |
| 1.75                 | 2.852                       | 0.457             | 0.326     | 0.425  | 98.97          | 308.63         |
| 2                    | 2.877                       | 0.457             | 0.330     | 0.434  | 96.74          | 304.59         |
| 2.25                 | 2.915                       | 0.457             | 0.335     | 0.446  | 94.21          | 298.88         |
| 2.5                  | 2.969                       | 0.457             | 0.339     | 0.461  | 90.94          | 313.06         |
| **2.75**             | **3.017**                   | **0.450**         | **0.346** | **0.469** | **86.71**     | **341.41**     |
| 3                    | 2.861                       | 0.411             | 0.323     | 0.381  | 90.61          | 237.26         |
this ohmic contact is responsible for eliminating the initial (in dry conditions) S-shaped I-V curve at $V_{oc}$ region.

The improvement in the solar cell can be observed with the improvement of the current-voltage characteristics. The initial S-shaped I-V curve with low solar cell parameters improves into one with significantly increased $I_{sc}$, $FF$ and $V_{oc}$, as it was mentioned earlier for different fullerene thicknesses. The device can be viewed as an OPV and supercapacitor connected in parallel via a common ion-porous MWCNT cathode. To maintain overall charge neutrality in the electrolyte, the negative ions ($\text{BF}_4$) move towards a MWCNT counter-electrode that is placed at the opposite side of the IL chamber, forming a second EDLC. The formation of the EDLC on the MWCNT counter-electrode is the charging voltage in the supercapacitor component of the structure. Formation of EDLC is expected to result in the n-doping of both the MWCNT electrode and the fullerene semiconductor, leading to the creation of ohmic contacts and n-i build-in junctions within the BHJ of CuPc/fullerene.

Summarizing, we have introduced here a concept of the "thick n-doped ETL based" ionically gated small molecule OPV. An electrolyte or ionic liquid in a microchamber is added on top of the cathode of OPV. Essential for this design is the existence of counter-electrode, which allows ions to diffuse into the ETL molecular layer and also it can be transparent for light (but not necessarily). In our proof of concept studies, we have used MWCNT as such a counter-electrode. In addition to the filling the earlier criteria, MWCNT can be easily doped by electrochemical double layer charging, which occurs naturally during the operation of the ionic-OPV structure. Ions from the ionic microchamber provide counter ions for EDLC charging, thus permitting both n-type doping (stabilized by in EDLC by positive ions of DEME) or p-type doping of counter-electrode (stabilized by negative ions in second EDLC). The organic layers adjacent to MWCNT cathode also are n-doped at higher $V_g$ in the properly built and operated device, and this doping provides not only a better ohmic contact between the doped MWCNT cathode and n-doped fullerene organic layer. This process reconfigures the OPV from undoped D-A type BHJ to n-i-i, or more
correctly heterojunction of the: A(n)-A(i)-D(i) type OPV with ohmic contacts to electrodes and internal built-in fields, increasing the performance.

Conclusions

We have demonstrated an effective tunable small molecule OPV structure with up to 200 nm-thick stable n-doped fullerenes (C$_{60}$ and C$_{70}$) ETL with a MWCNT cathode. This structure shows an improvement of all PV parameters $V_{oc}$, $I_{sc}$ and $FF$ leading to more than 50-time increase in PCE upon optimal ionic gating. Such operation is usually achieved with very thin intrinsic fullerene layer of 7 to 10 nm.

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