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Cobaltocene-Doped Viologen as Functional Components in Organic Electronics

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Given the energy level alignment between viologen and cobaltocene, cobaltocene readily transfers electrons to the intrinsically insulating viologen, resulting in the formation of an electron transfer complex with high electron density. When cobaltocene−viologen is incorporated as active layers in organic thin-film transistors, the output current of devices scales with increasing cobaltocene concentrations. We further demonstrate that cobaltocene−viologen makes effective electron transport layers in inverted polymer solar cells.

Introduction

The ability to controllably enhance charge transport in organic semiconductors via doping has garnered a lot of scientific attention.[1−8] In diodes and photovoltaic devices, doping of organic semiconductors can significantly increase current densities.[9,10] Similar processes have been shown to dramatically improve carrier mobility in organic thin-film transistors.[11] In inorganics, doping entails the introduction of electron donors and acceptors as dopants to generate loosely bound electrons and holes, respectively, for enhanced charge transport. Doping of organics, however, is different, and frequently requires the partial reduction or oxidation of the host material to increase electron and hole transport, respectively. For successful n-doping to occur, the dopant must possess sufficiently low ionization energy for efficient electron transfer to the host organic material. The energetic requirements thus mandate n-dopants to be inherently unstable and susceptible to oxidation.[1,12−14] As such, n-doping is significantly more challenging compared to p-doping of organics.

Viologen, of various salt forms, has been used as effective electron transfer catalysts and electron mediators during photosynthesis and photochemical studies.[15−18] From the standpoint of doping, viologen has been incorporated in fractional amounts in organic semiconductors of furazano(3,4-b)piperrazine, FP,[9] and poly(*p*-phenylene vinylene), PPV,[10] to improve hole transport. Both FP and PPV exhibit p-characteristics; incorporation of viologen abstracts electrons ($V^{+\bullet}$ in Scheme 1), thereby increasing hole transport in the host organic semiconductors. More recently, viologen has been added to carbon nanotubes to increase electron transport.[19] In this case, viologen is intentionally reduced to its neutral state (V in Scheme 1); exposure to a carbon nanotube matrix abstracts electrons from viologen and returns it to its charged states ($V^{+\bullet}$ and V^{++} in Scheme 1). In this process, the carbon nanotubes are reduced; thin-film transistors comprising treated carbon nanotubes exhibit stable n-characteristics up to 80 days.

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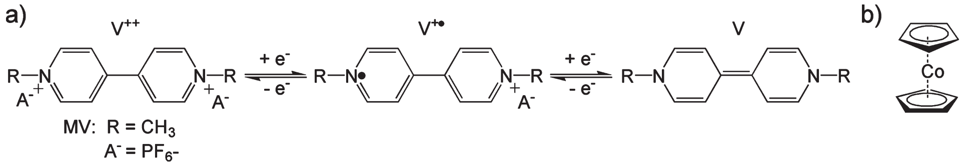
Scheme 1. (a) Chemical Structures of Viologen at Various Oxidation States[a] and (b) Chemical Structure of Cobaltocene



[a] The transparent insulating form of viologen is denoted V^{++}, transferring one electron to V^{++} results in $V^{+\bullet}$; the transfer of a second electron results in the formation of neutral viologen, V. MV is the PF_6^- salt of methyl viologen used in this study.

In the studies mentioned above, viologen plays the role of a dopant, either abstracting electrons from or donating electrons to the host organic semiconductor. Given the wide availability of viologen derivatives and the ease with which it accepts electrons, we explored the possibility of converting viologen, inherently an insulator with a band gap of 4 eV,[20] into an electrically active material that can be incorporated as functional components in electronic devices. Herein, we report the successful doping of viologen with cobaltocene, effectively rendering viologen electrically conductive. We further demonstrate the versatility and utility of cobaltocene−viologen by incorporating it as the active layer in organic thin-film transistors and as the electron transport layer in inverted polymer solar cells.

Experimental Section

Materials. The PF_6^- salt of 1,1′-dimethyl-4,4′-bipyridinium (methyl viologen, MV^{++} in Scheme 1) was obtained by metathesis with NH_4PF_6 (Alfa Aesar) as reported previously.[21] $MVCl_2$ (Aldrich) was dissolved in water, and a solution of excess NH_4PF_6 was added to precipitate $MV(PF_6)_2$. The white solid was filtered by vacuum filtration, washed with water, and recrystallized from ethanol/water. Bis(cyclopentadienyl)cobalt(II), or cobaltocene, was used as purchased from Sigma-Aldrich. We used anhydrous acetonitrile (99.8%, Sigma-Aldrich) and toluene ($\geq$99.5% ACS-grade reagent, also Sigma-Aldrich) to make test solutions for cyclic voltammetry experiments. Ferrocene (98%, Acros Organics) and tetrabutylammonium hexafluorophophate ($\geq$99.0%; Fluka) were added to test solutions as internal standard and electrolyte, respectively.

Characterization. UV−vis−NIR spectroscopy of solutions of viologen (MV^{++}; 17 mM) and cobaltocene (42 mM) and cosolutions of viologen and cobaltocene (total concentration 30 mM; viologen and cobaltocene added in equimass) in acetonitrile was acquired on an Agilent 8453 spectrophotometer from 280 to 1100 nm with a 1-nm resolution. Acetonitrile was used as background. Cyclic voltammetry was conducted on a CHI-660 electrochemical workstation (CH-Instruments). The test solution consisted of MV^{++} dissolved in 80:20 (v/v) toluene and acetronitrile at 0.25 mM. Tetrabutylammonium hexafluorophosphate, $(nBu)_4NPF_6$, was added as the electrolyte yielding a 0.1 M concentration in the test solution. A total of 5 μL of 110 mM ferrocene in acetonitrile was added as internal standard to 10 mL of test solution, resulting in a final concentration of 0.055 mM ferrocene. We also measured the electrochemical characteristics of a cosolution of cobaltocene and viologen. Viologen was kept at the same concentration, and we added cobaltocene to yield a cosolution with 72 mol % cobaltocene (0.64 mM cobaltocene). We used a glassy carbon (GC) working electrode, a platinum-wire counter electrode, and a silver/silver nitrate reference electrode (all purchased from CH-Instruments). The scan rate was 100 mV/s.

Device Fabrication and Testing. Organic thin-film transistors comprising MV^{++} and cobaltocene, as well as cobaltocene−viologen active layers, were fabricated in the bottom-contact geometry. Highly doped silicon with 300 nm thermal grown silicon dioxide (University Wafers) acted as the gate electrode and gate dielectric, respectively. A total of 2 nm of titanium and 50 nm of gold were deposited via electron-beam evaporation through a shadow mask to define the channel of the transistors (L = 600 μm and W = 4000 μm). After gold deposition, the substrates were cleaned by exposure to UV−ozone for 10 min, and the SiO_2 surface was treated with hexamethyldisilazane. The substrates were then transferred into a nitrogen-filled glovebox for the deposition of the active layer from 1 wt % solutions of viologen, cobaltocene, or mixtures thereof at varying molar ratios in acetonitrile. The current−voltage (I−V) characteristics of the transistors were acquired with an Agilent 4145B parameter analyzer. Inverted bulk heterojunction polymer solar cells were fabricated on prepatterned ITO-coated glass substrates that were cleaned in an ultrasonic bath using acetone, isopropyl alcohol, and deionized water. Viologen and cobaltocene dissolved at varying molar ratios in acetonitrile resulting in a 1 wt % solution were spin coated on the precleaned, patterned ITO-glass substrates at 4500 rpm for 30 s as the electron transport layer. To form the photoactive layer, poly(3-hexylthiophene), P3HT (Merck Chemicals Ltd.), and a fullerene derivative of [6,6]-phenyl-C_{61}-butyric acid methyl ester, PCBM (American Dye Source, Inc.), were first dissolved at equimass ratio in chlorobenzene to yield a 2.4 wt % solution, and the solution was spin coated directly on the electron transport layer. The coated substrates were then heated at 150 °C for 1 min, resulting in a 180 nm thick photoactive layer. The devices were then transferred from a nitrogen atmosphere to an evaporator outside the glovebox for electrode deposition. A total of 80 nm of gold was deposited on the photoactive layer via thermal evaporation through a shadow mask to form the top electrode. An array of seven individually addressable devices, each having an active area of 0.0635 cm^2, was fabricated on each patterned substrate. Immediately after gold evaporation, the devices were transferred back into the glovebox for testing. The current density−voltage ($J-V$) characteristics of these solar cells were measured using a Keithley 2400 source measurement unit under AM 1.5G 100 mW/cm^2 illumination.

Results and Discussion

Figure 1 shows the UV−vis−NIR spectra of solutions of pure viologen and cobaltocene, as well as a cosolution of viologen and cobaltocene (72 mol % cobaltocene). Viologen, in its stable doubly charged state (MV^{++}), does not absorb in the UV−vis−NIR range. Cobaltocene absorbs in the blue portion of the visible spectrum;

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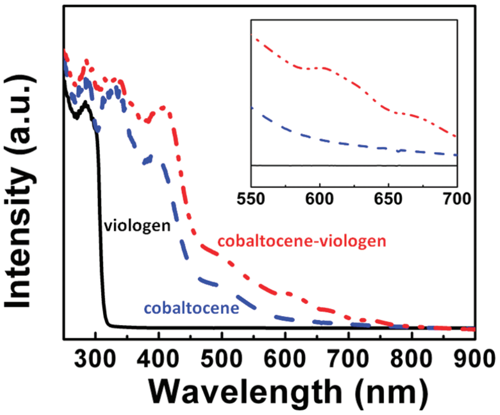

Figure 1. UV−vis−NIR absorption spectra of solutions of viologen, cobaltocene, and a cosolution of viologen and cobaltocene in acetonitrile. The inset shows the magnified region between 550 and 700 nm.

we observe strong absorptions between 400 and 550 nm. The spectrum of the cosolution appears similar to that of cobaltocene, with the exception of additional absorbances beyond 600 nm. The absorbances with λ_{max} at 603 and 660 nm are uniquely assigned to $MV^{+\bullet}$, the radical cation state of viologen (once reduced from the stable doubly charged state, MV^{++}).[20] The presence of these absorbances suggests electron transfer from cobaltocene to MV^{++}, resulting in the concomitant oxidation of cobaltocene and the reduction of MV^{++} to $MV^{+\bullet}$. We are not able to detect the presence of oxidized cobaltocene given that the UV−vis spectrum of oxidized cobaltocene does not show any absorbances beyond that exhibited by neutral cobaltocene.[22]

Figure 2 shows the cyclic voltammograms (CVs) of viologen (solid line) and a cosolution of cobaltocene and viologen (72 mol % cobaltocene; dashed dotted line). Ferrocene was added as internal standard in this experiment. Starting at zero potential, the voltage was first swept toward reducing potentials (negative voltages) and then cycled back to oxidizing potentials (positive voltages). The voltage was continuously cycled three times; the CV of viologen is not different on repeated cycling, offering evidence that it is stable and does not undergo degradation in the potential range examined. The redox couple with half potential ($E_{1/2}$) at 0.16 V vs Ag/AgNO$_3$ is attributed to the reduction (positive currents; peak potential 0.13 V) and oxidation (negative currents; peak potential 0.19 V) of ferrocene. The other two couples are attributed to the reduction and oxidation of viologen. Specifically, the first couple with $E_{1/2}$ at −0.69 V is associated with the conversion of MV^{++} to $MV^{+\bullet}$ (positive currents; peak potential −0.72 V) and vice versa (negative currents; peak potential −0.65 V) while the second couple with $E_{1/2}$ at −1.12 V is attributed to the further reduction (from $MV^{+\bullet}$ to MV; peak potential −1.16 V) and oxidation (from MV to $MV^{+\bullet}$; peak potential −1.07 V) of viologen. Given the onset of the first reduction peak of viologen (−0.60 V), we estimated the lowest unoccupied molecular orbital (LUMO) level of viologen to be 4.0 eV based on the onset of the oxidation peak of ferrocene (0.24 V) and its published HOMO value of 4.8 eV.[23,24] The CV of the cosolution appears to be similar to that of viologen. Given that the first redox couples in the CVs of viologen and cobaltocene−viologen are at the same potential, we concluded that the addition of cobaltocene does not alter the LUMO level of viologen. The presence of cobaltocene in the cosolution is only evident in a slight shift and an enhanced peak current of the second redox couple in the CV as the redox transition between Co^{2+} and Co^{3+} occurs in this vicinity as well.[25]

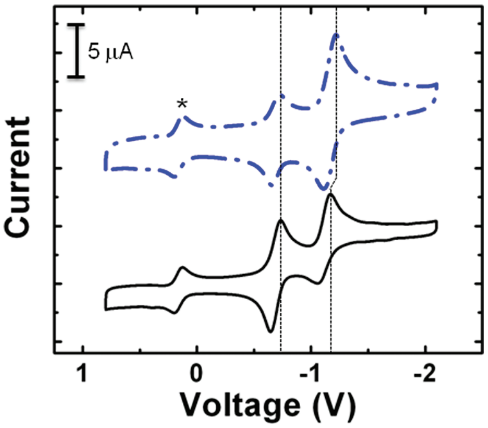

Figure 2. Cyclic voltammogram of viologen (solid line) and a cosolution of cobaltocene and viologen (72 mol % cobaltocene; dashed dot line). Ferrocene was added as the internal standard in this experiment. The redox couple of ferrocene is indicated by *.

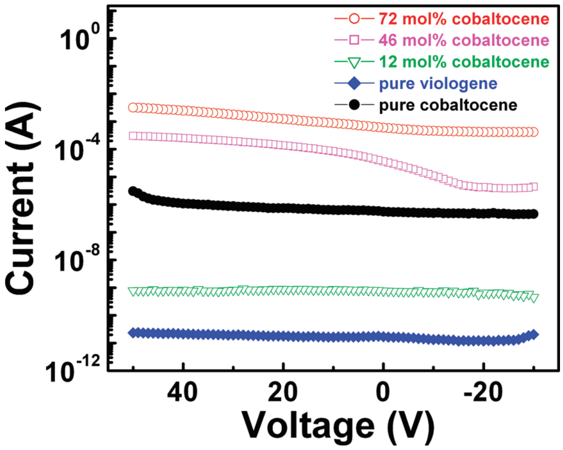

Figure 3. Transfer characteristics of organic thin-film transistors with active layers comprising viologen, cobaltocene, and cobaltocene−viologen at varying concentrations of cobaltocene.

Our characterization thus far has pointed out that cobaltocene, given its low electron affinity of 1.5 eV,[13] can transfer electrons to viologen, resulting in the formation of $MV^{+\bullet}$ that should be capable of electron transport. To assess the effectiveness with which cobaltocene donates electrons to viologen, we have fabricated and tested thin-film transistors comprising cobaltocene−viologen

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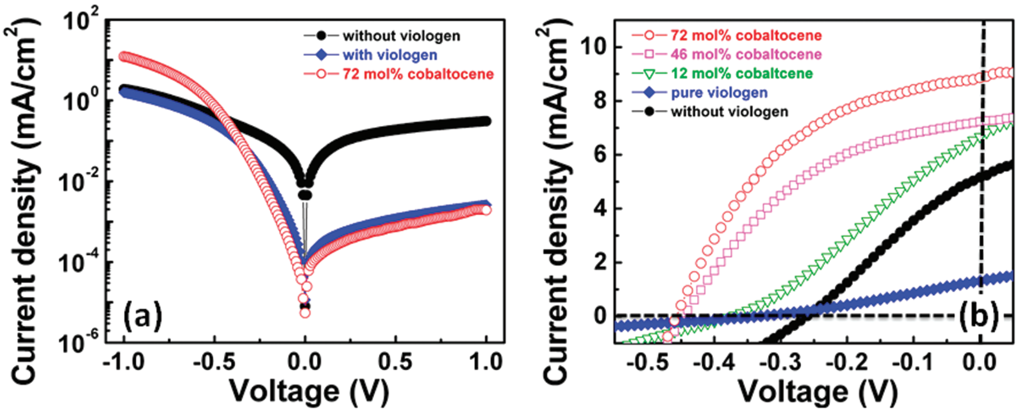

Figure 4. $J-V$ characteristics (a) in the dark and (b) under illumination (100 mW/cm^2) of inverted bulk-heterojunction polymer solar cells with electron transport layers comprising viologen and cobaltocene−viologen at varying concentrations.

as the active layer. Figure 3 shows the transfer characteristics of bottom-contact organic thin-film transistors in which the active layers comprise viologen with varying molar concentrations of cobaltocene. To obtain the transfer characteristics shown in Figure 3, we swept the gate voltage from −30 V to +50 V while holding the source−drain voltage constant at 50 V. The device comprising pure viologen exhibits extremely low current that is field independent (10^{-11} A). Given that the stable form of viologen (MV^{++}) is insulating, it is not surprising that we observe such low levels of current. Devices with pure cobaltocene also exhibit field-independent transfer characteristics; current levels on the order of 10^{-6} A are recorded. Devices comprising cobaltocene−viologen exhibit current levels that increase with increasing cobaltocene concentrations. In particular, the device with 12 mol % cobaltocene in the viologen active layer exhibits current levels that are 2 orders of magnitude higher than the device with pure viologen. Increasing the cobaltocene concentration further (46 mol % cobaltocene) yields a device that exhibits weak field dependence (on/off current ratio of 10^2). Further increasing cobaltocene concentration to 72 mol % within the active layer continues to increase the device current levels; currents as high as 10^{-2} A were recorded. Our CV experiments with cosolutions of cobaltocene and viologen suggest that electron transfer from cobaltocene to viologen increases the electron density in the conduction band of MV$^{+\bullet}$ without altering the energy levels of viologen.[13,14] As such, viologen exhibits two discrete electronic states. MV^{++} is intrinsically an insulator with a large band gap. The incorporation of cobaltocene results in the formation of MV$^{+\bullet}$ and transfers electrons into the conduction band of viologen. At sufficiently high electron density, MV$^{+\bullet}$ behaves like a conductor.

With the ability to produce conductive viologen films via the formation of electron transfer complex between viologen and cobaltocene, we wanted to assess the utility of such conductive films as candidates for electron transport layers in inverted polymer solar cells. Previously, we have demonstrated sol−gel processed titania to be effective electron transport layers in inverted polymer solar cells.[26,27] Because of shallow traps that are present in titania, however, devices with titania electron transport layers exhibit interesting transient photovoltaic behavior during initial testing.[27] Only when these shallow electron traps are filled and the photoconductivity of titania is saturated do we observe photovoltaic characteristics that are representative of the photoactive layer. In the present study, we have replaced sol−gel processed titania with cobaltocene−viologen as the electron transport layer in our inverted polymer solar cells. For comparison, we have also fabricated inverted polymer solar cells without any electron transport layer as well as those with pure viologen as the electron transport layer. Figure 4a contains the diode characteristics of three representative inverted solar cells acquired in the dark. The inverted polymer solar cell without any electron transport layer exhibits $J-V$ characteristics with little rectification ($< 10^2$ at ±1 V). This observation is not uncommon; the absence of a buffer layer selective for electrons permits the transport of holes in addition to electrons to the cathode. Further, it necessitates direct contact between the photoactive layer and the rough ITO surface, which frequently results in high leakage currents. The device with pure viologen as the electron transport layer shows markedly improved rectification (10^3 at ±1 V). The improvement in rectification stems from a decrease in the leakage current; the current level on forward bias remains the same compared to the device without any electron transport layer. We attribute this decrease in leakage current to the insertion of a buffer layer; albeit electrically inactive, it eliminates direct contact between the photoactive layer and ITO. The device with cobaltocene−viologen as the electron transport layer exhibits the best diode characteristics. We observe high rectification, at 10^4 at ±1 V with high current levels on forward bias. Given that cobaltocene−viologen has a high electron density and a decent conductivity, it selectively transports electrons while blocking the transport of holes during device operation.

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Table 1. Photovoltaic Characteristics of Inverted Polymer Solar Cells with Various Electron Transport Layers

	J_{SC} (mA/cm^2)	V_{oc} (V)	fill factor	efficiency (%)	series resistance ($\Omega \cdot$cm^2)
without viologen	5.32 ± 0.69	0.25 ± 0.04	0.28 ± 0.07	0.38 ± 0.17	28.85 ± 6.03
pure viologen	1.08 ± 0.07	0.34 ± 0.03	0.23 ± 0.03	0.08 ± 0.02	309.11 ± 11.93
12% mol cobaltocene	3.75 ± 0.11	0.35 ± 0.01	0.27 ± 0.02	0.22 ± 0.21	90.82 ± 19.88
21% mol cobaltocene	6.50 ± 0.41	0.37 ± 0.01	0.31 ± 0.04	0.49 ± 0.16	35.15 ± 7.09
46% mol cobaltocene	7.47 ± 0.20	0.44 ± 0.02	0.44 ± 0.06	1.38 ± 0.15	18.44 ± 2.15
72% mol cobaltocene	9.01 ± 0.33	0.46 ± 0.01	0.45 ± 0.05	1.92 ± 0.09	16.40 ± 0.81
pure cobaltocene	3.88 ± 0.29	0.18 ± 0.02	0.24 ± 0.03	0.17 ± 0.10	98.17 ± 7.36

Figure 4b contains the photovoltaic characteristics of inverted polymer solar cells under illumination. The average photovoltaic parameters along with standard deviations from the four to five devices measured are tabulated in Table 1. Without any electron transport layer, the inverted polymer solar cell exhibits poor device characteristics. The average short-circuit current density (J_{sc}) of such devices is 5.32 ± 0.69 mA/cm^2. The average open-circuit voltage (V_{oc}) is 0.25 ± 0.04 V. With an average fill factor of 0.28 ± 0.07, the average efficiency of such devices is merely 0.38 ± 0.17%. Insertion of viologen as the electron transport layer degrades the photovoltaic characteristics mainly through a decrease in J_{sc}. Given the insulating nature of MV^{++}, its incorporation in the charge transport pathway increases the series resistance of the device dramatically; the average series resistance extracted from devices with MV^{++} as the electron transport layer is 309 ± 11.93 $\Omega \cdot$cm^2 (extracted from the $J-V$ characteristics between the range of -0.9 to -1.0 V; data acquired in 0.01 V increments), as opposed to 28.85 ± 6.03 $\Omega \cdot$cm^2 in devices without any electron transport layer. This increase in series resistance leads to a dramatic decrease in J_{sc}. The incorporation of cobaltocene within viologen increases its electron density, effectively decreasing the series resistance and increasing the current density in our inverted polymer solar cells (Table 1). We observe a concomitant increase in V_{oc} when cobaltocene–viologen is used as the electron transport layer. Devices with 72 mol % cobaltocene exhibits an average J_{sc} of 9.01 ± 0.33 mA/cm^2 and an average V_{oc} of 0.46 ± 0.01 V. Given a markedly improved average fill factor of 0.45 ± 0.05, we observe an accompanying improvement in the average device efficiency (1.92 ± 0.09%). This increase in V_{oc} likely stems from changes in the electric field distribution within the device,[28] which in turn promotes more efficient charge carrier extraction. Unlike in common organic photovoltaic devices where the Fermi level is frequently pinned at the electron acceptor/cathode interface,[27] the increase in V_{oc} suggests that the Fermi level of viologen actually can shift toward its LUMO level on doping, resulting in better energy alignment at the electron extraction interface.

For completeness, we have also fabricated and tested inverted polymer solar cells with cobaltocene as the electron transport layer. These devices perform poorly; the average device characteristics are compiled in Table 1. The series resistance in these devices is high, resulting in low J_{sc}. The V_{oc} is especially low (0.18 ± 0.02 V), likely due to poor energy level alignment between the LUMO level of cobaltocene (1.5 eV)[15] and that of PCBM (3.7 eV).[29]

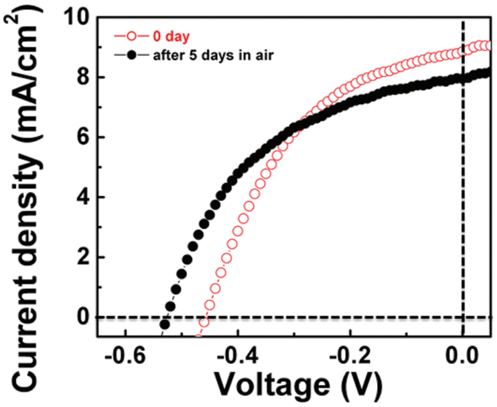

Figure 5. $J-V$ characteristics of inverted organic solar cells with cobaltocene–viologen (72 mol % cobaltocene) as the electron transport layer immediately after device fabrication and upon 5-day storage in air.

Finally, we examined the air stability of our best performing inverted polymer solar cell after it had been exposed to air for five days. The $J-V$ characteristics of a representative inverted polymer solar cell with cobaltocene-doped viologen (72 mol % cobaltocene) as the electron transport layer acquired immediately in the glovebox after device fabrication (open circles) and acquired after storage in air (filled circles) are shown in Figure 5. On storage, we observe a slight decrease in J_{sc}, likely due to oxidative degradation of the radical cation species of viologen (MV$^{+\bullet}$).[30] We note, however, that this reaction is not immediate; a 5-day exposure to air reduces the J_{sc} by less than 10%. Perhaps more dramatic is the increase in V_{oc} from 0.46 V to 0.53 V on storage in air. Such an increase has previously been attributed to oxygen doping of P3HT.[27,31]

Conclusion

Exposing viologen, an inherent transparent insulator, to cobaltocene enables the formation of an electron transfer complex, MV$^{+\bullet}$, that exhibits greatly enhanced conductivity. When incorporated as the active layer in an organic thin-film transistor platform, cobaltocene–viologen exhibits current levels that are weakly modu-

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lated by a gate bias. On the other hand, these films make effective electron transport layers in inverted polymer solar cells, facilitating more efficient collection of electrons at the cathode.

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