

Air-stable ambipolar organic transistors

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The authors report on ambipolar organic transistors based on the soluble dithiolene derivative (diphenylethylenedithiolato)(1,3-dithiol-2-thione-4,5-dithiolato)nickel [Ni(dpdt)(dmit)]. Due to its small band gap, efficient injection of holes and electrons from gold source/drain electrodes is possible. Both carrier mobilities are estimated to be approximately equal with maximum value on the order of 10^{-4} cm²/V s. The transistors exhibit excellent ambient stability with a shelf lifetime exceeding 3 months. The pronounced stability of Ni(dpdt)(dmit) as well as of several other molecules studied here is correlated to their redox potential. The present findings can be used as a general guide towards design and synthesis of air-stable ambipolar/*n*-channel molecules. © 2007 American Institute of Physics. [DOI: 10.1063/1.2715028]

Ambipolar charge transport in organic semiconductors is an interesting material property both for fundamental research and for technological applications. In recent years ambipolar transport has been exploited in organic field-effect transistors (OFETs) for the fabrication of complementary logic circuits¹⁻⁵ and bifunctional devices such as light-emitting OFETs.⁶⁻⁹ The majority of ambipolar organic transistors demonstrated so far are based on bulk heterojunction systems where an electron transporting (*n*-channel) material is mixed/blended with a hole transporting (*p*-channel) one, either through solution blending^{1,2} or thermal coevaporation,⁸ to form the heterogeneous ambipolar semiconductive layer. Bilayer-type ambipolar organic transistors based on the *p/n* heterostructure concept have also been demonstrated.¹⁰ Realization of ambipolar organic OFETs based on a single semiconductor, on the other hand, has been proven to be much more difficult mainly due to the poor environmental stability of the *n*-channel operation.^{1,5,9,11,12} Only recently single component air-stable ambipolar OFETs and logic circuits have been demonstrated.^{4,13} In these studies the near infrared absorbing dithiolene derivative bis[4-dimethylaminodithiobenzyl]-nickel was employed as the semiconductor layer. In spite of the very promising preliminary results, however, new ambipolar molecules with comparable environmental stability have yet to be demonstrated. To this end the synthesis of such molecules is of primary importance.

Here, we extend our previous work on air-stable ambipolar organic transistors and we report on devices based on the dithiolene derivative diphenylethylenedithiolate (diphenylethylenedithiolato)(1,3-dithiol-2-thione-4,5-dithiolato)nickel [Ni(dpdt)(dmit)]. Despite the fact that semiconductor deposition and transistor characterization are performed under ambient air and light, no degradation on device performance is observed for an exposure period of 3

months. The latter is attributed to the high electron affinity of Ni(dpdt)(dmit), making it less susceptible to atmospheric oxidants. The present findings can be viewed as a significant step toward designing and synthesis of environmentally stable molecules for application in organic electronics.

Field-effect transistors were made using heavily doped *p*-type Si wafers as the common gate electrode with a 200 nm thermally oxidized SiO₂ layer as the gate dielectric. Using conventional photolithography, gold source and drain electrodes were defined in a bottom-contact configuration with channel width (*W*) of 1000 μm and length (*L*) in the range 0.75–40 μm. A 10 nm titanium was used as an adhesion interlayer for the gold on SiO₂. Then, SiO₂ was treated with the primer hexamethyldisilazane prior to semiconductor deposition in order to passivate its surface. Films of Ni(dpdt)(dmit) were then drop cast on top of the prepatterned transistor substrates from a 1 mg/ml dichloromethane solution. Electrical measurements were performed in ambient conditions at room temperature using an HP 4156C semiconductor parameter analyzer.

The organometallic complex Ni(dpdt)(dmit) (Fig. 1, inset) was prepared by the cross-coupling-type method¹⁴ using the ligands diphenylethylenedithiolate (dpdt) (Ref. 15) and 1,3-dithiol-2-thione-4,5-dithiolate (dmit) (Ref. 16) in the presence of NiCl₂. The required asymmetrical complex was separated from the symmetrical by-products, namely, Ni(dpdt)₂ and Ni(dmit)₂, by liquid column chromatography. The latter is a dark-green microcrystalline material with melting point of >240 °C and molecular weight of 496.6. Furthermore, it is found to be soluble in CH₂Cl₂, CS₂, and various other organic solvents with a strong absorption band (in CS₂ solution) at 974 nm.¹⁷ Figure 1 shows the optical absorption spectrum for a spin coated film of Ni(dpdt)(dmit) deposited on quartz substrate directly from a CS₂ solution. From the onset of the absorption in the solid film, the optical band gap can be approximated, yielding a value of 0.85 eV. The redox potentials for Ni(dpdt)(dmit) were also measured, yielding $E_{1/2}(2-/1-)= -0.497$ V and $E_{1/2}(1$

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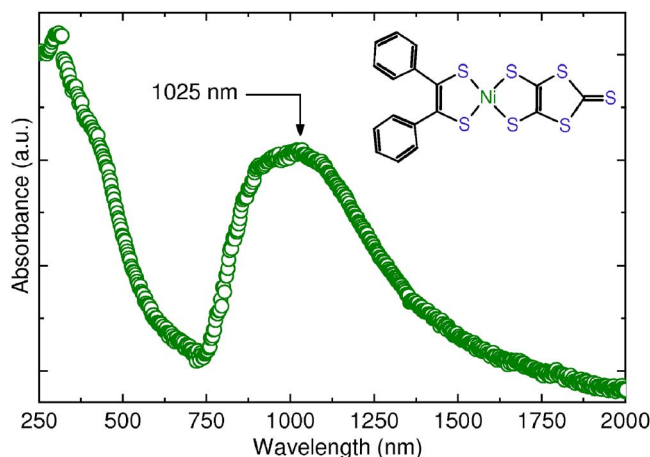


FIG. 1. (Color online) Absorption spectra of a Ni(dpdt)(dmit) film spin coated on quartz substrate from a CS₂ solution. Inset: Molecular structure of the Ni(dpdt)(dmit) derivative.

$-/0)=0.122$ V in CH₃CN vs saturated colomel electrode (SCE), respectively.^{18,19} By combining the optical and electrochemical data, the energy levels of the lowest unoccupied molecular orbitals (LUMOs) and highest occupied molecular orbitals can be estimated,^{20–23} yielding 4.43 and 5.28 eV, respectively.

To test the potential of Ni(dpdt)(dmit) for practical transistor applications, we have fabricated and characterized a number of bottom-contact OFETs. Figure 2 shows the output characteristics obtained from an OFET ($L=10$ μ m and $W=10$ mm) fabricated and characterized in ambient conditions. Despite the device exposure to air, strong hole and electron accumulation is observed under appropriate biasing conditions. In particular, for negative drain (V_D) and gate (V_G) voltages, accumulation of holes is evident. From these curves a maximum hole mobility of approximately 10^{-4} cm²/V s was derived. When V_D and V_G are biased positively, electron accumulation occurs with a maximum calculated mobility on the order of 3×10^{-4} cm²/V s. The on-off current ratio, calculated from the transfer characteristics of our best performing devices, is on the order of 10^2 – 10^3 . This relatively low value is ascribed to the characteristically small band gap (~ 0.85 eV) of Ni(dpdt)(dmit) that affect the

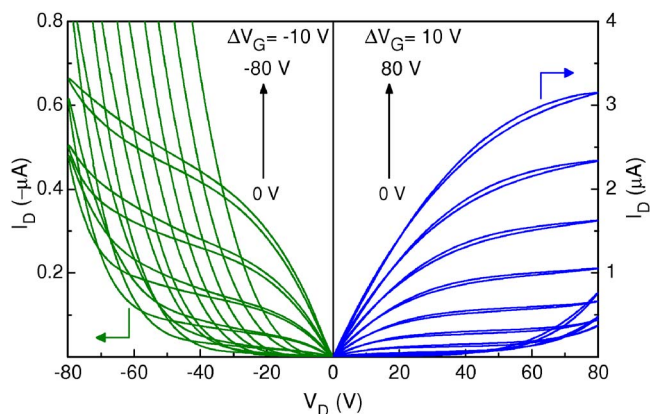


FIG. 2. (Color online) Output characteristics of a Ni(dpdt)(dmit) transistor with channel length and width of $L=10$ μ m and $W=10$ mm, respectively. Electrical characterization was performed in ambient conditions at room temperature. We note that the electrical characteristics remain the same even after exposure of the device to ambient atmosphere (shelve storage) for a period of 3 months.

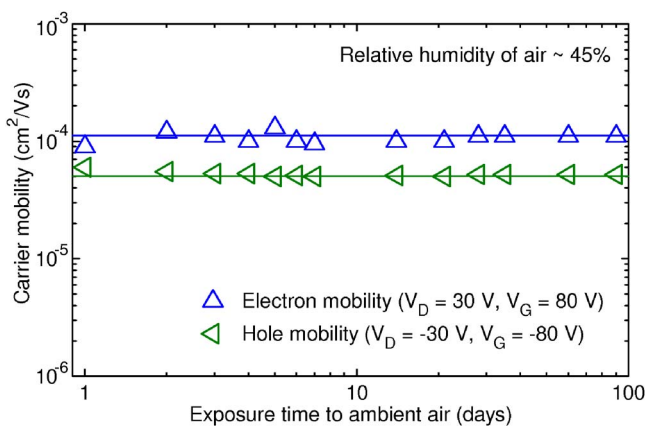


FIG. 3. (Color online) Hole and electron mobilities calculated in the saturation regime vs exposure time of the Ni(dpdt)(dmit) transistor to ambient air and light. Relative humidity of the ambient air was measured at approximately 45%.

switching characteristics of the transistors due to significant ambipolar carrier injection and transport through the channel. Moreover, from the linear dependence of I_D on $|V_D|$, observed at low bias, we conclude that gold electrodes provide nearly Ohmic contact for both hole and electron injections. The latter is attributed to the small band gap of Ni(dpdt)(dmit). Furthermore, the devices exhibit minimal hysteresis without noticeable changes before (tested in high vacuum) and after exposure to ambient air.

Despite the low carrier mobility values, the apparent environmental stability of the Ni(dpdt)(dmit) transistors is unprecedented. This is clearly demonstrated in Fig. 3, where the mobility of holes and electrons, calculated at $V_G = \pm 80$ V and $V_D = \pm 30$ V, is plotted versus exposure time to ambient air (i.e., shelve storage without any electrical bias applied) at a relative humidity of 45%. As can be seen no noticeable degradation on either electron or hole mobility is observed. Although the stability of the p -channel does not come as a surprise the n -channel stability does as it has been reported only for a handful of organic molecules.^{4,13,24–27} In an effort to elucidate the origin of the n -channel stability we have studied a series of organic molecules with different electrochemical characteristics (Fig. 4). Our results indicate that molecules with LUMO energies higher than approximately 4 eV (blue arrow) are far less sensitive to atmospheric air than molecules characterized by a lower LUMO (green arrow). In particular, we found that C₆₀ and C₇₀ fullerene derivatives, such as [6, 6]-phenyl-C₆₁-butyric acid methyl ester and [6, 6]-phenyl-C₇₁-butyric acid methyl ester, as well as pristine C₆₀, all with LUMOs < 4 eV, are highly sensitive to atmospheric air.^{3,11} On the contrary, molecules with LUMOs > 4 eV, such as [6, 6]-phenyl-C₈₅-butyric acid methyl ester,²⁷ dithiolenes derivatives,⁴ and perfluorinated copper phthalocyanine,²⁴ exhibit high n -channel stability. Our observation not only holds for the molecules shown in Fig. 4 but is also valid for most air-stable n -channel organic semiconductors reported in the literature, e.g., naphthalene/perylene derivatives,²⁵ cyano-polycyclic organic semiconductors,²⁶ and various others.

The critical issue of environmental stability of n -channel organic semiconductors has been initially addressed by de Leeuw *et al.* back in 1997.²⁸ In this early study the workers have identified oxygen (O₂) and water (H₂O) as the main atmospheric oxidants responsible for n -channel degradation

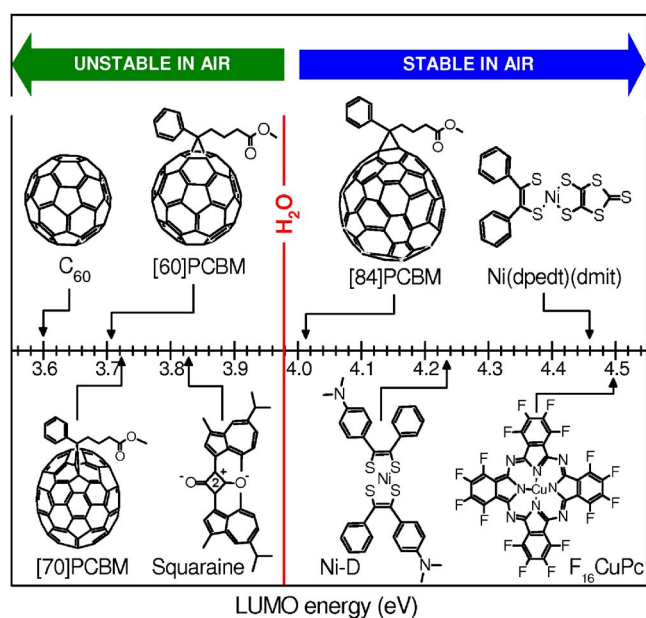


FIG. 4. (Color online) LUMO energy levels of the various organic molecules studied. The red line located at an energy level of 3.98 eV indicates the calculated redox potential (-0.658 V vs SCE) for water reduction at a $\text{pH}=7$ (Ref. 28). The green arrow indicates the LUMO energy range for unstable n -channel molecules toward ambient air. The blue arrow indicates the LUMO energy range for air-stable n -channel molecules. As can be seen a good agreement between theoretical prediction and the experimental results is observed.

upon exposure to atmospheric air. Specifically, they have calculated the limits of the reduction potential at which a n -channel molecule becomes unstable toward reduction of O_2 and H_2O . By assuming H_2O ($\text{pH}=7$) to be the main atmospheric oxidant contributor, this redox limit was calculated, yielding -0.658 V versus SCE. This potential can be translated to an electron affinity of approximately 4 eV (red line in Fig. 4), implying that molecules with LUMO < 4 eV are expected to be unstable toward reduction of H_2O due to the redox reaction. Under these circumstances H_2O molecules act as electron traps, thus reducing the electron current that flows through the channel. This prediction is in good agreement with our experimental findings presented in Fig. 4.

So far we have not been able to determine whether the instability of the n -channel molecules investigated here is solely due to H_2O or due to a combination of more atmospheric oxidants, i.e., O_2 , hydrogen peroxide, ozone, etc., and is beyond the scope of the present study. Further work, currently under way, is focusing on addressing this issue by looking on the relation between the electron affinity of various n -channel molecules and the electrochemical characteristics of individual atmospheric oxidants and their effects on device performance during shelf storage but also under continuous operating conditions (i.e., under bias stressing).

In summary, we have demonstrated ambipolar OFETs based on a soluble dithiolene derivative. Although the carrier mobilities in this particular molecule are moderate, the environmental stability of the OFETs, and particularly the n -channel operation, is unprecedented. Based on this result together with further experimental data obtained from several different organic semiconductors, we were able to correlate the n -channel stability of these molecules to their electrochemical characteristics. Our findings are inline with

earlier predictions on the effects of atmospheric oxidants²⁸ and suggest that for the synthesis of air-stable n -channel materials one must aim for organic molecules with electron affinity > 4 eV.

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