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Joon Hak Oh, Peng Wei, and Zhenan Bao

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Molecular n-type doping for air-stable electron transport in vacuum-processed n-channel organic transistors

Joon Hak Oh,^{1,2} Peng Wei,¹ and Zhenan Bao^{1,a)}

¹Department of Chemical Engineering, Stanford University, 381 North South Mall, Stanford, California 94305, USA

²School of Nano-Bioscience and Chemical Engineering, Ulsan National Institute of Science and Technology, Ulsan Metropolitan City 689-798, Republic of Korea

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The effects of n-type doping on the air-stability of vacuum-processed n-channel organic transistors have been investigated using perylene diimides and pyronin B as the active layer and dopant, respectively. Systematic studies on the influence of doping location revealed the n-type doping of bulk active layer or channel region significantly improves air-stability by compensating for the trapped electrons with the donated mobile electrons. Although n-type doping at the electrode contact could readily turn on the devices, it could not confer air-stable electron transport. The described approach would open up opportunities to enable and improve the stability of n-channel organic transistors in air. © 2010 American Institute of Physics. [doi:10.1063/1.3527972]

Controllable and stable doping of organic semiconductors allows reduction of Ohmic loss in transport layers, easier carrier injections from contacts, and tunable built-in potentials of Schottky or p-n junctions.¹ Recently, doping concepts applied in organic semiconductor devices have yielded high-performance organic light-emitting diodes² and organic photovoltaics.³ The p-type molecular doping has been frequently investigated using strong acceptors like tetrafluorotetracyanoquinodimethane (F₄-TCNQ).^{4–6} On the contrary, n-type molecular doping is more challenging because the dopants need to have a highest occupied molecular orbital (HOMO) level higher than the lowest unoccupied molecular orbital (LUMO) level of the matrix material, which makes them vulnerable to ambient oxidants.

Current approaches to n-type doping include: (i) use of alkali metal atoms,^{7,8} (ii) synthesis and/or search for compounds with extremely high-lying HOMOs,^{9,10} (iii) utilization of cationic salts which act as stable precursors for strong molecular donors,^{11–13} and (iv) molecular design of a reduced analog of the host molecule, so that the dopants do not disrupt the crystalline order.¹⁴ Ahles *et al.*⁸ reported n-type conduction of pentacene by interfacial doping with a Ca layer. Harada *et al.*¹⁵ demonstrated p-n homojunctions of zinc-phthalocyanine (ZnPc) using F₄-TCNQ acceptor and bis(terpyridine)ruthenium(II) ([Ru(terpy)₂]⁰) donor. pyronin B (PyB) chloride, employed in the third concept, has been reported to act as an excellent n-type dopant for 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTCDA).^{11–13} However, these n-type conductions were only observed under inert atmospheres, such as in N₂ or vacuum. For instance, the conductivity of PyB-doped NTCDA was drastically reduced upon exposure to air, presumably due to the charge trapping by oxygen.¹¹ For transistor applications, it is also desirable to get a reasonably low off-current from the doped system together with an improved on-current to achieve high on-to-off current ratios ($I_{\text{on}}/I_{\text{off}}$).

The number of air-stable high-performance n-type organic semiconductors is still less than that of p-type.¹⁶ None-

theless, they are indispensable for building complementary circuits which offer desirable advantages, such as low power consumption, high operating speed, and device stability. Recently, we have developed an approach to enable air-stable solution-processed n-channel organic thin-film transistors (OTFTs) by n-type doping.¹⁷ We found 4-(1,3-dimethyl-2,3-dihydro-1H-benzimidazole-2-yl)-phenyl-dimethyl-amine (N-DMBI) (Ref. 18) is able to act as an effective solution processable n-type dopant and offers significant improvement in the air-stability of N-DMBI doped [6,6]-phenyl C₆₁ butyric acid methyl ester (PCBM) OTFTs.¹⁷

Here we investigate the effects of n-type doping on the air-stability of vacuum-processed n-channel OTFTs by changing the doping location. Two n-channel semiconductors, namely, *N,N'*-dibutyl-1,7-difluoroperylene-3,4:9,10-tetracarboxylic diimide (F-PTCDI-C4) and *N,N'*-ditridecyl-perylene-3,4:9,10-tetracarboxylic diimide (PTCDI-C13), were chosen as the active materials for two reasons: (i) both exhibit excellent electron mobilities only under an inert atmosphere^{16,19} and (ii) both have LUMO levels (−3.76 and −3.70 eV for F-PTCDI-C4 and PTCDI-C13, respectively) right above the empirical onset region (−3.8 to −4.0 eV) observed for air-stability of arylene diimide-based n-channel OTFTs.²⁰ We employed a previously reported cationic dye, PyB, as the dopant because it is stable in air and commercially available.^{11–13} The chemical structures of the dopant and semiconductors are shown in Fig. 1.

PyB chloride and PTCDI-C13 were purchased from Acros and Aldrich, respectively, and F-PTCDI-C4 was synthesized as reported previously.¹⁶ TFT devices were prepared on a highly n-doped Si wafer with a thermally grown SiO₂ layer (300 nm). The SiO₂ surface was treated with *n*-octadecyltriethoxysilane (OTS) as described previously.²¹ For bulk doping, active layer (45 nm) was vacuum-deposited by coevaporation of the dopant and semiconductor (doping ratio 1:42) (Ref. 11) at a substrate temperature of 110 °C. For channel doping, PyB layer with a nominal thickness of 5 nm was deposited onto OTS-treated SiO₂, and then 45-nm-

^{a)}Electronic mail: zbao@stanford.edu.

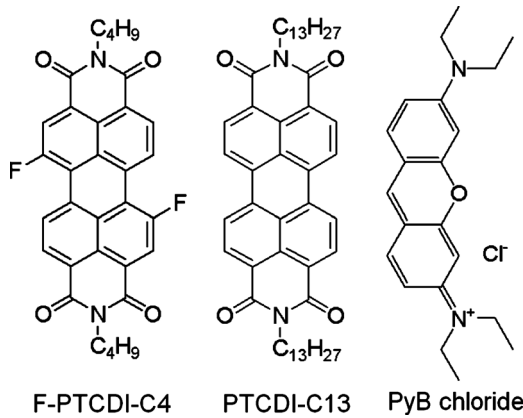


FIG. 1. Chemical structures of F-PTCDI-C4, PTCDI-C13, and PyB chloride.

thick PTCDI layer was deposited. For contact doping, PyB thin layer (5 nm) was deposited before the deposition of source and drain electrodes using the same shadow mask. Finally, Au source-drain electrodes (channel length and width: 50 μm and 1 mm) were thermally evaporated. The air exposure time of the semiconductor thin films was less than 5 min during the device fabrication. TFT characteristics were measured in both N_2 and air. The device structures are illustrated in Fig. 2.

Figure 3(a) exhibits the typical transfer characteristics of PyB-doped F-PTCDI-C4 TFTs in N_2 . Under an inert atmosphere, mobilities of 0.2 to 0.3 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ were obtained with an $I_{\text{on}}/I_{\text{off}}$ of $\sim 10^6$, regardless of the doping positions. However, the threshold voltage (V_T) shifted negatively by n-type doping, making it easier to switch on the devices. The contact-doped TFT exhibited the largest V_T shift owing to the significantly reduced energetic barriers for charge injection. After exposure to air for 1 h, the on-current of undoped F-PTCDI-C4 TFTs decreased considerably by two orders of magnitude, presumably due to oxygen trapping [Fig. 3(b)]. The contact-doped TFT also showed one order of magnitude drop in on-current. However, F-PTCDI-C4 TFTs prepared by bulk doping or channel doping exhibited the same order of on-current in air compared to that in N_2 . For all devices, the off-current decreased by approximately one order of magnitude after exposure to air. This led to a high $I_{\text{on}}/I_{\text{off}}$ ($\sim 10^7$) for both bulk and channel doped devices. The lower off-current in air is related to the oxidation of some doped PTCDI radical anions.¹⁹ The air-stability of PyB-doped F-PTCDI-C4 TFTs was investigated by monitoring the per-

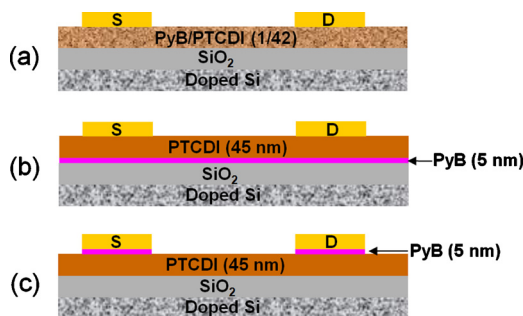


FIG. 2. (Color online) PyB-doped PTCDI TFT structures with different doping locations: (a) bulk doping, (b) channel doping, and (c) contact doping.

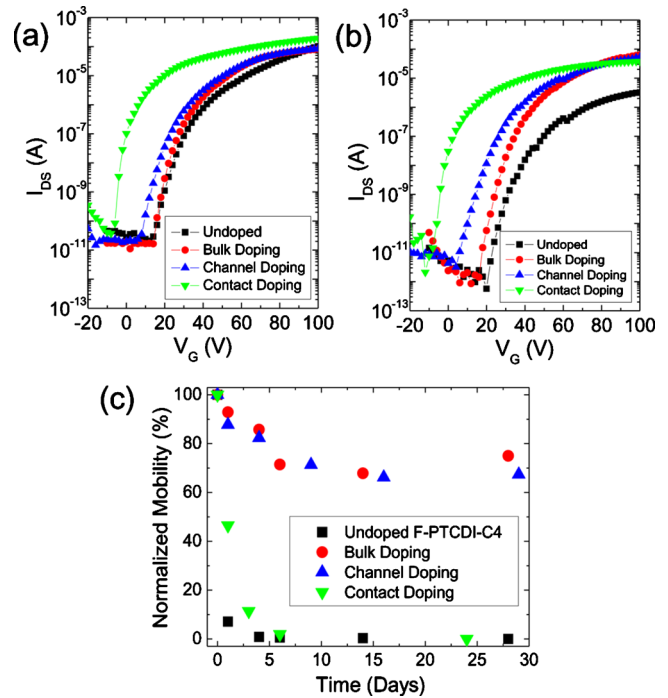


FIG. 3. (Color online) Current-voltage characteristics and air-stability measurements for PyB-doped F-PTCDI-C4 OTFTs. [(a) and (b)] Transfer characteristics at $V_{\text{DS}}=+100$ V (a) in a N_2 -filled glove-box and (b) in air (~ 1 h exposure). (c) Comparison of the normalized field-effect mobilities as a function of time for the pristine and doped devices.

formance of the devices stored in air as a function of time [Fig. 3(c)], without applying a continuous bias. The mobilities in air were normalized by those in N_2 . The performance of undoped F-PTCDI-C4 TFT degraded immediately after exposure to air, while the contact-doped F-PTCDI-C4 TFT was functional initially, but degraded after several days. However, the air-stability of F-PTCDI-C4 TFTs, prepared by either bulk doping or channel doping, improved significantly as $>60\%$ of the initial mobility in N_2 was retained. These results indicate that n-type doping of organic semiconductors, in particular the n-type doping in the charge transport pathways, can compensate for the trapped electrons. On the other hand, contact doping can reduce the energetic barriers of charge injection and transport. However, charge trapping in the channel region is still the major factor for air-stability.

To investigate if this doping approach is applicable to other organic semiconductors, we also explored the n-type doping of PTCDI-C13 TFTs. Although PTCDI-C13 TFT was reported to exhibit high mobilities up to 2.1 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, the device operation again diminishes rapidly in air.²² For the undoped PTCDI-C13 TFTs, we prepared PTCDI-C13 thin films with different thicknesses (45 and 100 nm) to see if increased film thickness, which slows down oxygen and water diffusion to the semiconductor/dielectric interface, will result in comparable stabilization as channel doping.²³ The channel-doped PTCDI-C13 TFTs operated in air with a mobility similar to that in N_2 (0.93 and 0.82 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ in N_2 and air, respectively) [Fig. 4(a)]. In N_2 , the $I_{\text{on}}/I_{\text{off}}$ was not high ($\sim 10^4$). However, when measured in air, it increased by more than one order of magnitude due to the lowering of the off-current while maintaining the high on-current, a trend similar to that observed for F-PTCDI-C4 TFTs. The performance of both the undoped PTCDI-C13 TFTs degraded rapidly in air, with the degradation of the 45-nm-thick TFTs

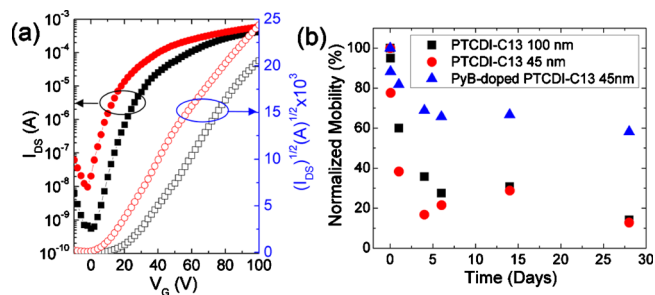


FIG. 4. (Color online) (a) Transfer characteristics of PyB channel-doped PTCDI-C13 TFTs in N₂ (circle) and air (rectangle, 1 h exposure). (b) Comparison of the normalized field-effect mobilities of pristine PTCDI-C13 TFTs with 100 and 45 nm thicknesses and PyB channel-doped 45-nm-thick PTCDI-C13 TFTs as a function of time.

being faster when compared to the 100-nm-thick TFTs [Fig. 4(b)]. In contrast, PyB-doped PTCDI-C13 TFTs showed a much improved stability in air compared to the undoped TFTs.

It has been previously reported that after heating and evaporation, the two species of PyB, i.e., the leuco- and neutral radical forms, are condensed into the thin films with the leucospecies as the major component.¹³ GAUSSIAN 03 (Ref. 24) calculations reveal the singly occupied molecular orbital (SOMO) level of the neutral radical of PyB to be -3.34 eV. Thus, the neutral radical species allows electron transfer from the PyB neutral radical to the PTCDis.¹³ It has also been proposed that the leuco-form itself cannot act as an n-type dopant because of its higher ionization potential, but electron transfer between the donor and the acceptor can take place by a hydride transfer.¹ Our findings indicate that if the mobile electrons generated by n-type doping are located abundantly in the bulk active layer or in the channel region, they can compensate for the trapped electrons to a significant degree, thereby improving their stability in air.

In summary, we have demonstrated that n-type doping by vacuum evaporation is an efficient approach to enable air-stable n-channel organic transistors. The n-type doping of bulk active layer or channel region improved the air-stability of PTCDI-based n-channel OTFTs while maintaining a high I_{on}/I_{off} . Although the n-type doping of electrode contact was helpful in lowering the turning-on voltage of the devices, it did not result in their stable ambient operation. Our approach should provide great opportunities for achieving air-stable n-channel OTFTs using organic semiconductors that were previously unstable in air.

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- ¹K. Walzer, B. Maennig, M. Pfeiffer, and K. Leo, *Chem. Rev. (Washington, D.C.)* **107**, 1233 (2007).
- ²S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lüssem, and K. Leo, *Nature (London)* **459**, 234 (2009).
- ³G. Schwartz, B. Maennig, C. Uhrich, W. Gnehr, S. Sonntag, O. Erfurth, E. Wollrab, K. Walzer, and M. Pfeiffer, *Proc. SPIE* **7416**, 74160K (2009).
- ⁴W. Gao and A. Kahn, *Appl. Phys. Lett.* **79**, 4040 (2001).
- ⁵Y. Zhang, B. d. Boer, and P. W. M. Blom, *Adv. Funct. Mater.* **19**, 1901 (2009).
- ⁶K.-H. Yim, G. L. Whiting, C. E. Murphy, J. J. M. Halls, J. H. Burroughes, R. H. Friend, and J.-S. Kim, *Adv. Mater. (Weinheim, Ger.)* **20**, 3319 (2008).
- ⁷G. Parthasarathy, C. Shen, A. Kahn, and S. R. Forrest, *J. Appl. Phys.* **89**, 4986 (2001).
- ⁸M. Ahles, R. Schmechel, and H. v. Seggern, *Appl. Phys. Lett.* **85**, 4499 (2004).
- ⁹A. Nollau, M. Pfeiffer, T. Fritz, and K. Leo, *J. Appl. Phys.* **87**, 4340 (2000).
- ¹⁰C. K. Chan, F. Amy, Q. Zhang, S. Barlow, S. Marder, and A. Kahn, *Chem. Phys. Lett.* **431**, 67 (2006).
- ¹¹A. G. Werner, F. Li, K. Harada, M. Pfeiffer, T. Fritz, and K. Leo, *Appl. Phys. Lett.* **82**, 4495 (2003).
- ¹²A. Werner, F. Li, K. Harada, M. Pfeiffer, T. Fritz, K. Leo, and S. Machill, *Adv. Funct. Mater.* **14**, 255 (2004).
- ¹³C. K. Chan, E.-G. Kim, J.-L. Brédas, and A. Kahn, *Adv. Funct. Mater.* **16**, 831 (2006).
- ¹⁴B. A. Gregg, S.-G. Chen, and H. M. Branz, *Appl. Phys. Lett.* **84**, 1707 (2004).
- ¹⁵K. Harada, A. G. Werner, M. Pfeiffer, C. J. Bloom, C. M. Elliott, and K. Leo, *Phys. Rev. Lett.* **94**, 036601 (2005).
- ¹⁶R. Schmidt, J. H. Oh, Y.-S. Sun, M. Deppisch, A.-M. Krause, K. Radacki, H. Braunschweig, M. Könemann, P. Erk, Z. Bao, and F. Würthner, *J. Am. Chem. Soc.* **131**, 6215 (2009).
- ¹⁷P. Wei, J. H. Oh, G. Dong, and Z. Bao, *J. Am. Chem. Soc.* **132**, 8852 (2010).
- ¹⁸X.-Q. Zhu, M.-T. Zhang, A. Yu, C.-H. Wang, and J.-P. Cheng, *J. Am. Chem. Soc.* **130**, 2501 (2008).
- ¹⁹J. H. Oh, S. Liu, Z. Bao, R. Schmidt, and F. Würthner, *Appl. Phys. Lett.* **91**, 212107 (2007).
- ²⁰B. A. Jones, A. Facchetti, M. R. Wasielewski, and T. J. Marks, *J. Am. Chem. Soc.* **129**, 15259 (2007).
- ²¹Y. Ito, A. A. Virkar, S. Mannsfeld, J. H. Oh, M. Toney, J. Locklin, and Z. Bao, *J. Am. Chem. Soc.* **131**, 9396 (2009).
- ²²S. Tatemichi, M. Ichikawa, T. Koyama, and Y. Taniguchi, *Appl. Phys. Lett.* **89**, 112108 (2006).
- ²³J. H. Oh, Y.-S. Sun, R. Schmidt, M. F. Toney, D. Nordlund, M. Könemann, F. Würthner, and Z. Bao, *Chem. Mater.* **21**, 5508 (2009).
- ²⁴M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Gaussian, Inc., Pittsburgh, PA, 2003.