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Air-stable *n*-channel organic thin-film transistors with high field-effect mobility based on *N,N'*-bis(heptafluorobutyl)-3,4:9,10-perylene diimide

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The thin-film transistor characteristics of *n*-channel organic semiconductor, *N,N'*-bis(2,2,3,3,4,4,4-heptafluorobutyl)-perylene tetracarboxylic diimide, are described. The slip-stacked face-to-face molecular packing allows a very dense parallel arrangement of the molecules, leading to field-effect mobility as high as $0.72 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The mobility only slightly decreased after exposure to air and remained stable for more than 50 days. Our results reveal that molecular packing effects such as close stacking of perylene diimide units and segregation effects imparted by the fluorinated side chains are crucial for the air stability. © 2007 American Institute of Physics. [DOI: 10.1063/1.2803073]

Fundamental interests in charge transport mechanisms and potential applications in large-area, low-cost, and flexible electronic systems have motivated the development of organic thin-film transistors (OTFTs).¹ While *p*-channel semiconductors have been studied extensively, *n*-channel semiconductors have been less exploited. Although rapid progress for *n*-channel semiconductors has been made over the past few years,^{2–12} many of the *n*-channel materials only work in vacuum or under an inert atmosphere, because ambient oxygen and moisture can act as electron traps. Considering practical applications such as *p-n* junctions, bipolar transistors, and complementary circuits, the development of air-stable high-performance *n*-channel semiconductors is very important.

Perylene diimides (PTCDI) are among the most promising *n*-channel candidates due to their high electron affinity and the large π -orbital overlap in the solid state.^{4,9–13} In contrast to their mother compound, perylene tetracarboxylic dianhydride (PTCDA),¹⁴ electron withdrawing substituents can be introduced at the imide nitrogens of PTCDI to stabilize field-induced electron transport by lowering the lowest unoccupied molecular orbitals (LUMO) of the resulting molecule.^{8,9,12} Recently, a PTCDI derivative bearing cyano substituents at the PTCDI core has been reported to provide solubility and air stability by lowering the LUMO level significantly to resist ambient oxidation.¹²

Here, we describe the electrical performance of *N,N'*-bis(2,2,3,3,4,4,4-heptafluorobutyl)-3,4:9,10-perylene tetracarboxylic diimide (PTCDI-C4F7) [Fig. 1(a)].¹⁵ The absence of core substituents makes the torsion of the PTCDI π system very small, and allows a very dense molecular packing, which leads to high charge carrier mobilities.

TFT devices were prepared on highly doped *n*-type Si wafers as a gate electrode with a thermally grown SiO₂ (300 nm, capacitance $C_i = 10 \text{ nFcm}^{-2}$) dielectric. The SiO₂

surface was treated with *n*-octadecyl triethoxysilane [C₁₈H₃₇Si(OC₂H₅)₃] (OTS) as described previously.⁹ PTCDI-C4F7 molecules were vacuum deposited at various substrate temperatures to form thin films (45 nm). Finally, Au source-drain electrodes (channel length and width: 100 μm and 2 mm, respectively) were thermally evaporated through a shadow mask. TFT characteristics were measured in a N₂-filled glove-box as well as under ambient environment at about 1 h after expose to air.

Table I summarizes the charge carrier mobilities (μ), on/off current ratios ($I_{\text{on}}/I_{\text{off}}$), and threshold voltages (V_t) as a function of substrate temperature (T_D). The mobilities were determined in the saturation regime from the slope of plots of $(I_{\text{DS}})^{1/2}$ vs V_{GS} . The highest level of mobilities was observed at a T_D of 125 °C. In N₂ atmosphere, 12 devices from

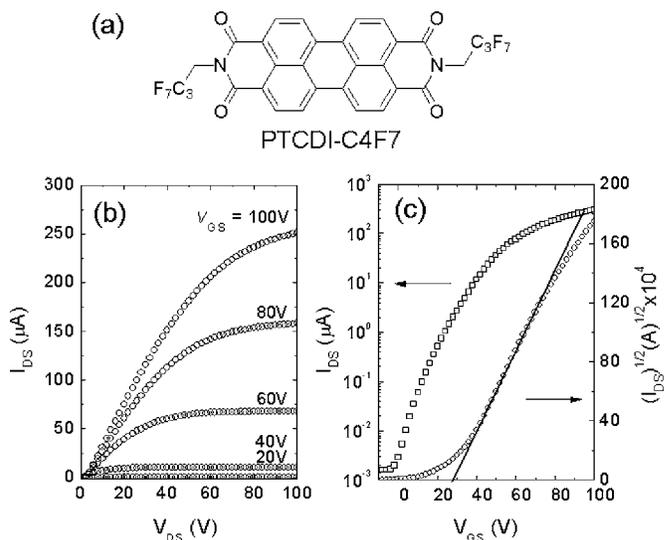


FIG. 1. (a) Chemical structure of PTCDI-C4F7. [(b) and (c)] Current-voltage characteristics for the PTCDI-C4F7 TFT prepared at $T_D = 125 \text{ }^\circ\text{C}$: (b) output characteristics and (c) transfer characteristics ($V_{\text{DS}} = +100 \text{ V}$). The measurement was conducted under nitrogen atmosphere.

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TABLE I. Summary of field-effect mobilities (μ), on/off ratios ($I_{\text{on}}/I_{\text{off}}$), and threshold voltages (V_t) for PTCDI-C4F7 TFTs prepared on OTS-treated substrates at various substrate temperatures (T_D).

T_D (°C)	In N_2 atmosphere			In ambient air		
	μ ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) ^a	$I_{\text{on}}/I_{\text{off}}$	V_t (V)	μ ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	$I_{\text{on}}/I_{\text{off}}$	V_t (V)
25	0.064 ± 0.004	$(5.3 \pm 4.2) \times 10^6$	9–24	0.053 ± 0.005	$(5.7 \pm 4.8) \times 10^5$	25–32
90	0.45 ± 0.05	$(5.8 \pm 3.1) \times 10^5$	12–28	0.34 ± 0.05	$(5.2 \pm 4.5) \times 10^5$	27–46
110	0.52 ± 0.03	$(6.5 \pm 4.5) \times 10^5$	15–28	0.43 ± 0.04	$(8.7 \pm 5.2) \times 10^5$	29–44
125	0.67 ± 0.05	$(7.5 \pm 6.3) \times 10^5$	14–29	0.51 ± 0.05	$(4.3 \pm 3.1) \times 10^6$	28–43
140	0.35 ± 0.04	$(4.1 \pm 2.8) \times 10^5$	7–21	0.27 ± 0.03	$(6.8 \pm 3.4) \times 10^5$	21–33

^aThe average values obtained for at least six devices from more than two different batches.

four different batches showed an average mobility of $0.67 \pm 0.05 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and $I_{\text{on}}/I_{\text{off}}$ greater than 10^5 . The output and transfer characteristics of a PTCDI-C4F7 TFT device with the highest mobilities are illustrated in Figs. 1(b) and 1(c), which correspond to a mobility of $0.72 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ with $I_{\text{on}}/I_{\text{off}}$ of 2.0×10^5 and V_t of 27 V. On the other hand, the mobility of PTCDI-C4F7 TFTs in air was $0.51 \pm 0.05 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ with $I_{\text{on}}/I_{\text{off}}$ of about 10^6 . The highest mobility in air was $0.56 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. It is remarkable that the PTCDI-C4F7 TFTs in air exhibit mobilities close to those in N_2 atmosphere, even though they do not have electron-withdrawing groups at the PTCDI core. The V_t increased in air as a result of oxygen (and moisture) traps.¹⁶ In the PTCDI-C4F7 TFT device shown in Fig. 1(c), the V_t shift of +10.4 V suggests that approximately additional specific charges of $1.04 \times 10^{-7} \text{ C cm}^{-2}$ (carrier density of $6.5 \times 10^{11} \text{ cm}^{-2}$) are trapped by exposing the film to air. The OTS-treated substrates showed one to three orders of magnitude higher mobilities compared to bare SiO_2/Si substrates. This is possibly attributed to the reduced charge trapping at the dielectric/semiconductor interface of OTS-treated substrates,^{2,9} although PTCDI derivatives are generally considered to be unaffected by silanol-type traps.^{4,17} Atomic force microscopy (AFM) analysis revealed that the grains on OTS-treated substrates are much larger and well-defined compared to those on bare substrates, which is consistent with higher mobility in the OTS-treated substrates.

Solvent-free single crystals of PTCDI-C4F7 were obtained by recrystallization from toluene and analyzed by x-ray diffraction (XRD). The crystal structure (triclinic space group $P-1$) reveals a slip-stacked face-to-face molecular packing with close contacts of 3.31 \AA between the PTCDI π planes. This value is smaller than those of dicyano-PTCDI (3.40 \AA) (Ref. 12) and alkyl-substituted PTCDis ($3.34\text{--}3.55 \text{ \AA}$),^{18,19} and is very close to the value of PTCDA (3.23 \AA) (Ref. 20) which lacks bulky imide substituent. The distortion of the PTCDI-C4F7 core amounts only to about 1.5° . This close distance of undistorted PTCDI cores allows a very dense and parallel arrangement of the molecules, which is desirable for high charge carrier mobility. The out-of-plane XRD measurements of the vapor-deposited thin films exhibit a sharp primary peak at $2\theta=5.54^\circ$, which corresponds to a d spacing of 15.94 \AA . Judging from a geometry-optimized, computed molecular length (21.78 \AA) of PTCDI-C4F7 molecule, the tilt angle relative to the substrate normal of 47° is obtained. This result suggests that PTCDI-C4F7 molecules have favorable molecular orientations for charge transport between source-to-drain electrodes.¹²

Figure 2 illustrates tapping-mode AFM images. As generally observed for organic semiconductors,^{1,9} AFM images reveal that the grain size becomes larger as the T_D increases, which is followed by increased mobilities. As seen from Table I, the mobility increased with the T_D and reached the maximum mobility at 125°C . As the temperature increased further, the mobility started to decrease. At 150°C , only several devices showed transistor behavior. This is likely due to the significantly increased gaps between the grains and crack formation in the films [Fig. 2(d)]. The terrace height determined by AFM is $16 \pm 1 \text{ \AA}$, which agrees well with the XRD peak.

The air stability of PTCDI-C4F7 TFTs was monitored by measuring the performance as functions of time (Fig. 3). The mobility decreased from 0.63 to $0.48 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ immediately after taking out the device from the glove box, but no further decrease was observed even after more than 50 days. The V_t increased right after expose to air, but stayed in between 35 and 50 V. The on/off ratios improved compared to that in the N_2 glove box, since the off current decreased by an order of magnitude in air. This is presumably due to the oxidation of unintentionally doped PTCDI radical anions in air.

The first reduction potential of PTCDI-C4F7, measured in dichloromethane by using cyclic voltammetry, was ob-

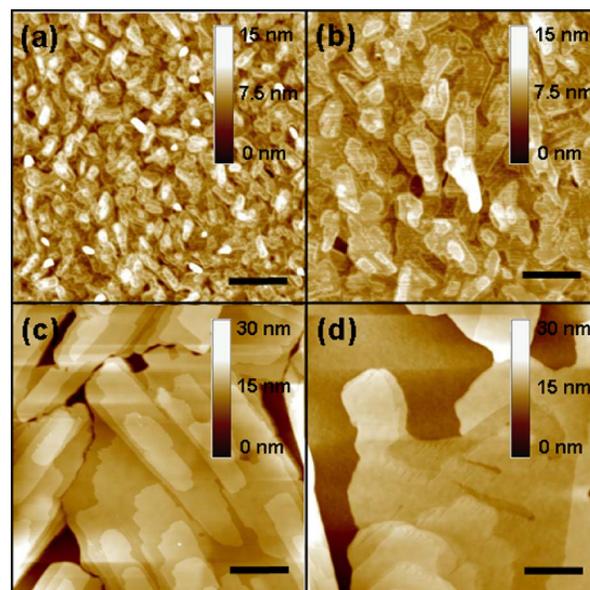


FIG. 2. (Color online) AFM topography images of PTCDI-C4F7 thin films deposited onto OTS-treated SiO_2/Si substrates at various substrate temperatures: (a) 25°C , (b) 90°C , (c) 125°C , and (d) 150°C . Scale bar: 400 nm.

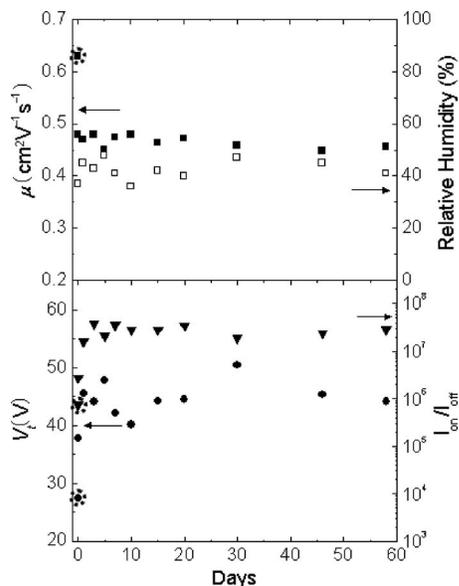


FIG. 3. Air-stability measurements of a PTCDI-C4F7 TFT. Top: μ (solid squares) and relative humidity (open squares). Bottom: V_g (circles) and I_{on}/I_{off} (triangles). The dotted circle values at initial time correspond to an electrical performance in a nitrogen glove box.

served at $E_{1/2}^1 = -0.95$ V versus ferrocene. Since the redox potential of ferrocene corresponds to -4.8 eV with respect to the vacuum level,²¹ this suggests a LUMO level of -3.85 eV for PTCDI-C4F7. This is quite high (about 0.35 – 0.45 eV) compared to other air-stable n -channel semiconductors such as dicyano-functionalized PTCDis (-4.2 to -4.3 eV).^{12,17} On the other hand, dialkyl-substituted PTCDis (Ref. 22) have a higher LUMO level of -3.70 eV, consistent with the fact that their TFT performances are unstable in air. A carbonyl-functionalized quaterthiophene with a LUMO level of -3.96 eV exhibits a high electron mobility (~ 0.6 cm² V⁻¹ s⁻¹) under vacuum, but degrades by an order of magnitude in air.²³ The other high-performance n -channel organic semiconductors are mostly defective in air and are much more difficult to obtain and purify with the exception of C₆₀.²⁴

Considering these electrochemical data, the air stability of PTCDI-C4F7 TFTs is thought to be strongly related with the molecular packing and morphology of the thin films.^{12,25–27} The densely packed PTCDI cores together with the closely packed fluorocarbon chains may provide a kinetic barrier to the diffusion of oxygen and moisture into the channel region. This result also suggests that attachment of additional electron-withdrawing groups at the PTCDI core, which always goes along with synthetic complexity, is not required to achieve air stability. The PTCDI-C4F7 might be a strong candidate for widely applicable n -channel materials, since it is easily accessible from commercially available PTCDA and the electrical performance is excellent.

In summary, we report an n -channel organic semiconductor based on bis(heptafluorobutyl)-substituted PTCDI with a charge carrier mobility as high as 0.72 cm² V⁻¹ s⁻¹. Very dense and parallel arrangement of undistorted PTCDI π planes facilitates charge carrier transport. The PTCDI-C4F7 TFTs exhibit long-term air-stable operation, despite the ab-

sence of electron-withdrawing substituent at the aromatic core and the relatively high LUMO level. Our results reveal that molecular packing effects and self-segregation of fluorinated side chains are crucial for air stability.

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¹Z. Bao and J. Locklin, editors, *Organic Field-Effect Transistors* (Taylor and Francis, Boca Raton, 2007).

²L.-L. Chua, J. Zaumseil, J.-F. Chang, E. C.-W. Ou, P. K.-H. Ho, H. Sirringhaus, and R. H. Friend, *Nature (London)* **434**, 194 (2005).

³H. E. Katz, A. J. Lovinger, J. Johnson, C. Kloc, T. Siegrist, W. Li, Y.-Y. Lin, and A. Dodabalapur, *Nature (London)* **404**, 478 (2000).

⁴R. J. Chesterfield, J. C. McKeen, C. R. Newman, P. C. Ewbank, D. A. S. Filho, J.-L. Brédas, L. L. Miller, K. R. Mann, and C. D. Frisbie, *J. Phys. Chem. B* **108**, 19281 (2004).

⁵A. Facchetti, M.-H. Yoon, C. L. Stern, G. R. Hutchison, M. A. Ratner, and T. J. Marks, *J. Am. Chem. Soc.* **126**, 13480 (2004).

⁶S. Tatemichi, M. Ichikawa, T. Koyama, and Y. Taniguchi, *Appl. Phys. Lett.* **89**, 112108 (2006).

⁷P. R. L. Malenfant, C. D. Dimitrakopoulos, J. D. Gelorme, L. L. Kosbar, and T. O. Graham, A. Curioni, and W. Andreoni, *Appl. Phys. Lett.* **80**, 2517 (2002).

⁸Z. Bao, A. Lovinger, and J. Brown, *J. Am. Chem. Soc.* **120**, 207 (1998).

⁹M.-M. Ling, P. Erk, M. Gomez, M. Koeneemann, J. Locklin, and Z. Bao, *Adv. Mater. (Weinheim, Ger.)* **19**, 1123 (2007).

¹⁰H. Z. Chen, M. M. Ling, X. Mo, M. M. Shi, M. Wang, and Z. Bao, *Chem. Mater.* **19**, 816 (2007).

¹¹R. Schmidt, M. M. Ling, J. H. Oh, M. Winkler, M. Köneemann, Z. Bao, and F. Würthner, *Adv. Mater. (Weinheim, Ger.)* **19**, 3692 (2007).

¹²B. A. Jones, M. J. Ahrens, M.-H. Yoon, A. Facchetti, T. J. Marks, and M. R. Wasielewski, *Angew. Chem., Int. Ed.* **43**, 6363 (2004).

¹³F. Würthner, *Chem. Commun. (Cambridge)* 2004 1564.

¹⁴S. R. Forrest, *Chem. Rev. (Washington, D.C.)* **97**, 1793 (1997).

¹⁵K. Deyama, H. Tomoda, H. Muramatsu, and M. Matsui, *Dyes Pigm.* **30**, 73 (1996).

¹⁶R. J. Chesterfield, J. C. McKeen, C. R. Newman, C. D. Frisbie, P. C. Ewbank, K. R. Rann, and L. L. Miller, *J. Appl. Phys.* **95**, 6396 (2004).

¹⁷B. Yoo, T. Jung, D. Basu, A. Dodabalapur, B. A. Jones, A. Facchetti, M. R. Wasielewski, and T. J. Marks, *Appl. Phys. Lett.* **88**, 082104 (2006).

¹⁸G. Klebe, F. Graser, E. Hädicke, and J. Berndt, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **B45**, 69 (1989).

¹⁹P. M. Kazmaier and R. Hoffmann, *J. Am. Chem. Soc.* **116**, 9684 (1994).

²⁰S. R. Forrest, M. L. Kaplan, and P. H. Schmidt, *J. Appl. Phys.* **55**, 1492 (1984).

²¹R. S. Ashraf, M. Shahid, E. Klemm, M. Al-Ibrahim, and S. Sensfuss, *Macromol. Rapid Commun.* **27**, 1454 (2006).

²²The reduction potentials ($E_{1/2}^{red}$) of PTCDI-C8 and other alkyl-substituted PTCDis measured under the same condition as for PTCDI-C4F7 correspond to -1.08 to -1.12 eV versus ferrocene.

²³M.-H. Yoon, S. A. DiBenedetto, A. Facchetti, and T. J. Marks, *J. Am. Chem. Soc.* **127**, 1348 (2005).

²⁴K. Itaka, M. Yamashiro, J. Yamaguchi, M. Haemori, S. Yaginuma, Y. Matsumoto, M. Kondo, and H. Koinuma, *Adv. Mater. (Weinheim, Ger.)* **18**, 1713 (2006).

²⁵H. E. Katz, J. Johnson, A. J. Lovinger, and W. J. Li, *J. Am. Chem. Soc.* **122**, 7787 (2000).

²⁶H. E. Katz, Z. Bao, and S. L. Gilat, *Acc. Chem. Res.* **34**, 359 (2001).

²⁷C. D. Dimitrakopoulos and P. R. L. Malenfant, *Adv. Mater. (Weinheim, Ger.)* **14**, 99 (2002).