

Naphthalenetetracarboxylic Diimide-Based n-Channel Transistor Semiconductors: Structural Variation and Thiol-Enhanced Gold Contacts

Howard E. Katz,* Jerainne Johnson,[†] Andrew J. Lovinger, and Wenjie Li[‡]

Contribution from Bell Laboratories, Lucent Technologies, 600 Mountain Avenue, Murray Hill, New Jersey 07974

Received March 10, 2000. Revised Manuscript Received June 13, 2000

Abstract: The synthesis and field-effect transistor (FET) electron mobility of ten N-substituted naphthalene 1,4,5,8-tetracarboxylic diimide (NTCDI) derivatives deposited at ambient and elevated temperatures are reported. Mobilities >0.01 cm²/(V s) were measured in air for three NTCDIs with partially fluorinated substituents, and >0.001 cm²/(V s) for a hydroxy-terminated compound. Mobilities 0.001–0.1 cm²/(V s) were also found for three *n*-alkyl NTCDIs, but only under vacuum; FET operation with gold bottom contacts was enabled by specific thiol coatings of the contacts. The highest mobility in air, >0.1 cm²/(V s), was conferred by 4-trifluoromethylbenzyl substitution, while 1*H*,1*H*-perfluorooctyl substitution resulted in an on/off ratio in air $>10^5$. Solution electrochemistry and solid-state X-ray and electron diffraction were employed to partially explain the results, and applications of the materials to complementary circuits are considered.

Field-effect transistors (FETs) with organic semiconductors as active materials are the key switching components of organic, or “plastic”-based control, memory, or logic circuits.¹ FETs are switched from the “off” to the “on” state by the creation of a channel of charge along a semiconductor–dielectric interface, controlled by a gate electrode. Current can then be passed between source and drain electrodes along the channel, with higher mobility correlating with higher current for a given geometry and quantity of injected charge.² The chief advantage envisioned for “plastic electronics” would be the availability of more facile fabrication methods compared to those commonly employed for traditional silicon technology, resulting in a cost advantage when the performance level and device density associated with silicon are not essential. Organic semiconductors are more likely to be printable than vapor-deposited inorganics, and could be less sensitive to air than recently proposed solution-deposited inorganics.³

The most power-efficient families of logic elements are so-called “complementary” circuits, requiring both electron-carrying (*n*-channel) and hole-carrying (*p*-channel) semiconductors.⁴ The vast majority of organic FET semiconductors, as well as the most convenient solution-deposited inorganic semiconductors, are *p*-channel, meaning that positive charge carriers can be injected and made to move through the material. *n*-Channel compounds, into which negative charge carriers can be injected and made mobile, are much rarer. The most useful is perfluorinated copper phthalocyanine (PFCP), which has a mobility of 0.02 cm²/(V s) and is stable in air, but requires

vacuum deposition on substrates heated above 100 °C.⁵ Other candidate materials, including C₆₀⁶ and naphthalene 1,4,5,8-tetracarboxylic dianhydride (NTCDA),⁷ cannot be used in air, and are also sparingly soluble. Recently, pentacene, which does not form air-stable solutions, has been shown to be both *n*- and *p*-channel.⁸ NTCDA has a fairly high on/off ratio as well as the additional advantage of transparency, but is saddled with a low mobility of 0.001 cm²/(V s).⁷

1,4,5,8-Naphthalenetetracarboxylic diimide (NTCDI) is similarly transparent, but has even lower mobility.⁷ However, because of the single-step synthesis available for NTCDI derivatives⁹ (Figure 1), it is possible to screen a large number of imide side chains for their impact on the NTCDI electronic properties, in the hope of improving mobility and environmental stability. In principle, one could vary chain lengths, degrees of unsaturation, functional group polarity, intramolecular binding and self-segregation activity, and even subsequent reactivity. For this study, we selected a minimal number of such groups to address the effects of alkyl chain length, benzyl and phenyl architecture, and incorporation of fluoro and oxygenated groups. These groups could influence performance through alteration of the naphthalenediimide orbital energies, admission or exclusion of electron-quenching species from the environment, and/or changes in the naphthalenediimide nearest neighbor interactions in the solid state. Device fabrication could also be affected through changes in the solubility or volatility of the compounds, ordering induced by the interaction of substituents with dielectric surfaces, and interactions between substituents and electrical contact materials.

[†] Summer Student 1999. Currently at University of Southern California.

[‡] Current address IBM Microelectronics, Hopewell Junction, NY 12533. Work done while at Bell Laboratories.

(1) Drury, C. J.; Mutsaers, C. M. J.; Hart, C. M.; Matters, M.; de Leeuw, D. M. *Appl. Phys. Lett.* **1998**, *73*, 108. Garnier, F.; Hajlaoui, R.; Yassar, A. *Science* **1994**, *265*, 1684.

(2) Katz, H. E.; Bao, Z. *J. Phys. Chem.* **2000**, *104*, 0000.

(3) Ridley, B. A.; Nivi, B.; Jacobson, J. M. *Science* **1999**, *286*, 746. Kagan, C. R.; Mitzi, D. B.; Dimitrakopoulos, C. D. *Science* **1999**, *286*, 945.

(4) Lin, Y.-Y.; Dodabalapur, A.; Sarpeshkar, R.; Bao, Z.; Li, W.; Baldwin, K.; Raju, V. R.; Katz, H. E. *Appl. Phys. Lett.* **1999**, *74*, 2714.

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

(6) Haddon, R. C.; Perel, A. S.; Morris, R. C.; Palstra, T. T. M.; Hebard, A. F.; Fleming, R. M. *Appl. Phys. Lett.* **1995**, *67*, 121.

(7) Laquindanum, J. G.; Katz, H. E.; Dodabalapur, A.; Lovinger, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 11331.

(8) Schön, J. H.; Berg, S.; Kloc, Ch.; Batlogg, B. *Science* **2000**, *287*, 1022.

(9) Rademacher, A.; Maerkle, S.; Langhals, H. *Chem. Ber.* **1982**, *115*, 2927.

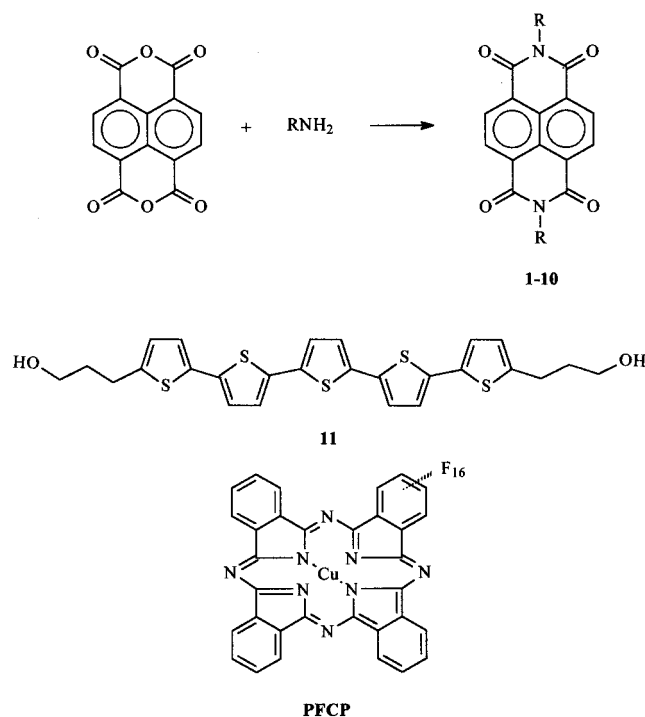


Figure 1. Synthesis and molecular structures of semiconductors used in this study.

FET mobilities and other performance parameters are generally assessed using the top contact FET geometry because the application of electrodes to the already deposited semiconductor film ensures intimate contact over much of the electrode area. However, to utilize these compounds in some circuit applications and test vehicles, it is desirable to employ the bottom contact geometry, even though contact may be limited to a fraction of the vertical wall area of the electrode. In this situation, increased contact resistance arising from interfacial charge migration, surface dipoles, the insulating nature of the side chains, or physical delamination would be much more significant.

One means of lowering the contact barrier between gold and organic semiconductor is to adsorb a polar thiol onto the gold prior to deposition of the semiconductor. The dipole moment associated with the adsorbate has been shown to modify the effective work function of the gold, and in favorable cases this could ease charge injection.¹⁰ It is not necessary that such improvements in contact properties be due specifically to surface dipoles. For example, any treatment that induces a favorable surface voltage drop by inducing charge carrier drift or band bending between the metal and semiconductor (as has been demonstrated for carboxylic acids on CdTe¹¹ and quinolinium ions on Si¹²) could be helpful, as could simple enhancements in semiconductor adhesion or molecular orientation relative to the metal. The hydrophobicity and surface electronic potential were simultaneously modified by the use of adsorbates on gold and CuInSe₂ with both dipolar and alkyl functionality.¹³ Preliminary results indicate that the adsorption of thiols on gold electrodes is beneficial for pentacene bottom-contact p-channel FETs, although the degree of performance enhancement and

Table 1. Substituents "R" and Synthesis Data for NTCDI Derivatives

compd no.	N-substituent	mol of amine/mol of NTCDA	mL of quinoline/g of NTCDA	% yield after sublimation
1	C ₈ F ₁₅ H ₂	3	15	37
2	C ₄ F ₇ H ₂	4	12	20
3	C ₈ H ₁₇	3	12	29
4	C ₁₂ H ₂₅	3	11	25
5	C ₁₈ H ₃₇	4	15	19
6	HOOC ₆ H ₁₂	3	3	11 ^a
7	C ₄ H ₉ OC ₃ H ₆	3	3	10 ^b
8	CF ₃ C ₆ H ₄ CH ₂	3	9	44
9	CH ₃ C ₆ H ₄ CH ₂	3	9	67
10	C ₆ F ₅	4	12	26

^a Elemental analysis indicated 0.5 equiv of included water. ^b Elemental analysis indicated 0.25 equiv of included water.

the mechanism by which it occurs have not been determined.¹⁴ Contact–semiconductor interfaces have also been modified by doping the semiconductor selectively in the near-contact region.¹⁵

This paper reports an expanded study of a series of sublimable NTCDI n-channel semiconductors. Some of these compounds are solution-processable, and some provide for device operation in air. Possible mechanisms by which the side chains influence device activity are considered, and methods for fabricating active bottom-contact devices are also elucidated. Some preliminary results have been reported in a communication.¹⁶

Experimental Section

Synthesis of NTCDI Derivatives. NTCDA, an excess of amine RNH₂, and about 0.7 mol equiv of zinc acetate were stirred in quinoline and the temperature was raised above 200 °C over several hours.⁹ The exact compounds and amounts used are listed in Table 1. The mixture was allowed to cool, and solids were collected and washed with hot dilute aqueous Na₂CO₃, water, and toluene. The remaining crude solid was sublimed under vacuum. Satisfactory elemental analyses were obtained, except as noted in Table 1. The synthesis of bis(2,2,2-trifluoroethyl)-NTCIDI from trifluoroethylamine hydrochloride and excess tertiary amine base was attempted, but was unsuccessful.

Synthesis of bis(3-hydroxypropyl)-a5T (11). 5-(3-Tetrahydropranyloxypropyl)-2,2'-bithiophene was converted to the 5'-tributylstannyl derivative and Stille-coupled to 2,5-dibromothiophene as previously described.¹⁷ Thermal deprotection occurred in boiling mesitylene. Vacuum sublimation then gave material with a satisfactory elemental analysis.

Other Materials. The various aromatic thiols (except for one compound noted below), mercaptopropylcarboxy derivatives, and sulfur were obtained from Aldrich and used as received. The polyimide dielectric was Amoco Ultradel, dissolved in γ -butyrolactone. BCB was obtained as a solution in mesitylene from Dow. The methacrylate dielectric was a synthesized 9:1 copolymer of methyl methacrylate and hydroxyethyl methacrylate, cross-linked with an aromatic diisocyanate. Carbon ink was obtained from SPI Supplies, division of Structure Probe International. Tetrabutylammonium hexafluorophosphate was recrystallized from THF. Ferrocene was used as received. 3,4-Dichlorobenzyl mercaptan was synthesized from the corresponding benzyl chloride by treatment with thiourea in refluxing ethanol, followed by hydrolysis in 10% aqueous NaOH at reflux, as previously described.¹⁸

Substrates and Procedures. Si wafers with 3000 Å of thermal oxide or other conductive substrates with spin-coated dielectrics were coated with semiconductors or gold at pressures below 10⁻⁵ Torr. A heated

(14) Jackson, T. *Proc. MRS* **1999**, Fall BB9.7.

(15) Hajlaoui, R.; Horowitz, G.; Garnier, F.; Arce-Bouchet, A.; Laigre, L.; El Kassmi, A.; Demanze, F.; Kouki, F. *Adv. Mater.* **1997**, *9*, 389.

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

(17) Li, W.; Katz, H. E.; Lovinger, A. J.; Laquindanum, J. G. *Chem. Mater.* **1999**, *11*, 458.

(10) Zehner, R. W.; Parsons, B. F.; Hsung, R. P.; Sita, L. R.; *Langmuir* **1999**, *15*, 1121.

(11) Cohen, R.; Bastide, S.; Cahen, D.; Libman, J.; Shanzer, A.; Rosenwaks, Y. *Opt. Mater.* **1998**, *9*, 394.

(12) Cohen, R.; Zenou, N.; Cahen, D.; Yitzchaik, S. *Chem. Phys. Lett.* **1997**, *279*, 270.

(13) Bruening, M.; Cohen, R.; Guillemoles, G.; Moav, T.; Libman, J.; Shanzer, A.; Cahen, D. *J. Am. Chem. Soc.* **1997**, *119*, 5720.

Table 2. Layer Spacings and FET Mobilities of NTCDI Semiconductors

compd no.	spacing (Å)	mobility, cm ² /(V s) (ambient T)	elevated T _{dep} (°C)	mobility, cm ² /(V s)	
				elevated T _{dep}	under vacuum
1	27	0.01	70	0.05	small decrease
2	17	0.01	70	(desorbed)	
3	23	10 ⁻⁶	70	10 ⁻⁶	0.16
4	30		50	<10 ⁻⁵	0.005–0.01
5	39		50	10 ⁻⁶	0.005
6	22		90	0.001	0.002
7	17		50	<10 ⁻⁶	<10 ⁻⁶
8	19	0.01	98	0.12	small increase
9	18		70	10 ⁻⁶	<10 ⁻⁵
10	amorphous	<10 ⁻⁶	70	<10 ⁻⁶	<10 ⁻⁶

stage was used to maintain elevated substrate temperatures during some semiconductor depositions. Carbon ink was painted with a brush. Thiols were deposited onto gold contacts in 0.1% ethanol solutions at room temperature. Thiols with 4-chloro groups tended to cause delamination of the gold after more than a few minutes, because of the lack of a metal glue layer. However, deposition for 3–5 min was sufficient for significant electrical contact effects to be observed. Oxygen plasma cleaning¹⁹ was conducted in a Technics Series 800 reactive ion etcher. X-ray diffraction and current–voltage data were obtained as previously reported.²⁰ Electrical characterization was generally done in air, except in specific experiments where an evacuated chamber was employed. Electrochemistry was performed in THF using platinum working and counter electrodes, and a silver–silver nitrate–acetonitrile reference electrode.

Results

With few exceptions, all of the NTCDI derivatives formed powders that displayed many X-ray diffraction peaks, and sublimed thin films of the compounds showed layer spacings consistent with the molecular lengths, allowing for a modest degree of tilting, and few if any other peaks. In some cases, several orders of the layer diffraction were observed. The layer spacings are listed in Table 2, and some illustrative examples of diffraction patterns are shown in Figure 2. Compound **10** and several other *N*-phenyl analogues that had been screened in the past were completely amorphous. Partially fluorinated compound **2** was somewhat less crystalline as a powder and room-temperature deposited film than the others, and the ordering was not as controlled by layering. Hydroxy compound **6** was generally less ordered than the others as judged by the increased breadth of X-ray diffraction peaks from films. Compound **7**, with the ether side chain, had a layer spacing considerably shorter than the presumed molecular length, indicating significant deviation from a fully extended conformation, or an unusually large tilt. Compound **8** was poorly crystalline when deposited at ambient temperature and as a singly sublimed powder, but highly crystalline when doubly sublimed or deposited at elevated temperature.

Films of compounds **1–3** were additionally characterized by electron diffraction and microscopy. The longer chain compounds produced sharp, discontinuous diffraction rings at angles corresponding to spacings much smaller than the layer spacings. The micrographs of the compounds, especially when deposited at elevated temperatures, were dominated by flat regions many microns on a side, consistent with the discontinuous rings. Compound **1** was coarser when deposited at ambient temper-

ature, and showed a second, ribbonlike morphology on top of the flat regions at 70 °C. The diffraction rings for compound **2** were much more diffuse. In general, the degree of ordering and the molecular length spacing did not seem to depend strongly on whether side chains were fluorinated or not.

Top contact gold device mobilities at ambient and elevated temperatures and effects of inert atmosphere on mobilities are also listed in Table 2. Only the three fluorinated compounds **1**, **2**, and **8** showed high mobilities in air after room-temperature deposition. The mobilities of compounds **1** and **8** were substantially higher on deposition at elevated temperatures, and the hydroxy compound **6** also had a measurable mobility as a higher temperature film. On/off ratios on the order of 10⁵ were achievable with **1** and **2**, although threshold voltages exceeded 20 V. Compound **3**, despite its high mobility, had a much lower on/off ratio, typically about 100 versus zero gate, although much higher when the device was turned off with depletion. The threshold voltage, however, was close to 10 V. Device characteristics of **1** and **8** are compared in Figure 3. Compound **2** was too volatile for deposition on heated substrates, and substantially desorbed when heated under high vacuum. All the other compounds showed mobilities at or below detection limits in air, although the long chain alkyl substituted NTCDI **3–5** had moderate to high mobilities in a vacuum. The compounds that had significant mobilities in air were little affected by vacuum.

To determine whether semiconducting activity of a hydroxy-alkyl compound would be restricted to electron transport, thiophene oligomer **11** was prepared and tested. The mobility, presumably arising from hole transport, was between 10⁻⁴ and 10⁻³ cm²/(V s).

Because of the exemplary behavior of compounds **1**, **2**, and **8**, devices using alternative configurations and processes were explored using them. Carbon electrodes gave similar but less reproducible mobilities than did gold electrodes with **1**, and mobilities with particularly thin gold electrodes were diminished and contact limited. Carbon also worked as a bottom contact source/drain material while bottom contact gold, even when cleaned with an oxygen plasma, generally failed (see below). Aluminum electrodes did not give active devices. The mobility of **1** was fairly insensitive to the degree of purity of the source material and the thickness of the sublimed film; a mobility of 0.04 cm²/(V s) was measured for a film of **1** sublimed from the crude reaction product without any prior sublimation, and 150 Å films gave mobilities nearly as high as 500 Å films. A mobility of 0.001 cm²/(V s) was reached with **1** on a BCB dielectric, and the film was highly ordered. The mobility of **2** on polyimide and on a cross-linked poly(methyl methacrylate) was 0.01 cm²/(V s). Compound **8** did not show significant mobility on polymer dielectrics. Devices were stable to repeated cycling in air for periods of up to an hour if voltages were kept under 50 V. Failure in some cases was due to contact delamination or rupture. It is anticipated that packaging the devices and use of higher capacitance dielectrics would greatly improve device stability.

As discussed in an earlier communication,¹⁶ devices could be fabricated from **1** by deposition of the semiconductor from an aromatic solvent. In addition, compound **6** is soluble and castable in *n*-butanol, a nonaromatic and less toxic solvent, and its OH groups (and those of **11**) could act as attachment sites for a biological molecule, as suggested previously for an amino-substituted thiophene derivative.²¹

Because some of the processes envisioned for manufacturing organic FET-based circuits require that source/drain electrodes

(18) Urquhart, G. G.; Gates, J. W., Jr.; Connor, R. *Organic Syntheses*; John Wiley: New York, 1955; Collect. Vol. III, p 363.

(19) Ron, H.; Rubinstein, I. *Langmuir* **1994**, *10*, 4566.

(20) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 664.

(21) Muguruma, H.; Saito, T.; Hiratsuka, A.; Karube, I.; Hotta, S. *Langmuir* **1996**, *12*, 1251.

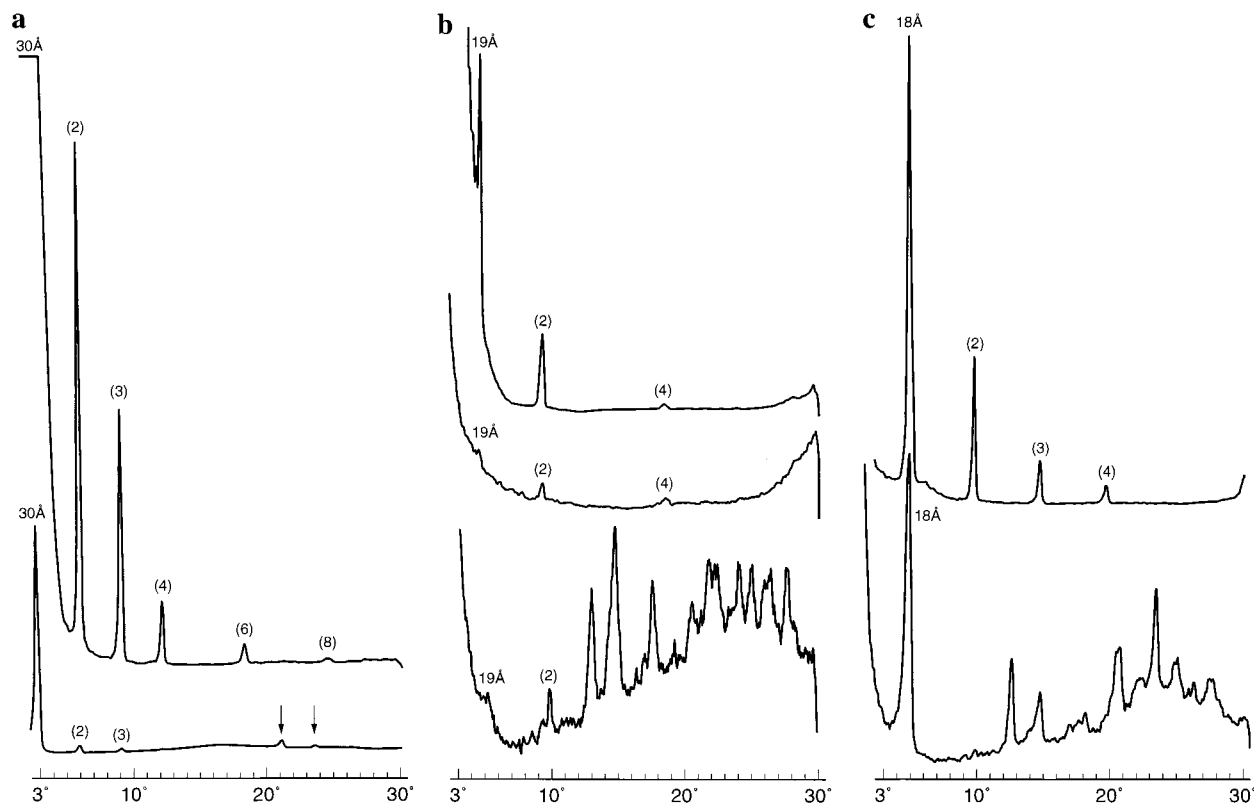


Figure 2. X-ray diffraction patterns of (a) powder (bottom) and 50 °C sublimed film (top) of **4**, (b) powder (bottom), 50 °C (middle), and 70 °C (top) sublimed films of **8**, and (c) powder (bottom) and ambient sublimed film (top) of **9**. The absence of peaks in the film patterns other than orders of layer diffraction indicates a layered morphology with molecular long axes roughly perpendicular to the substrate plane.

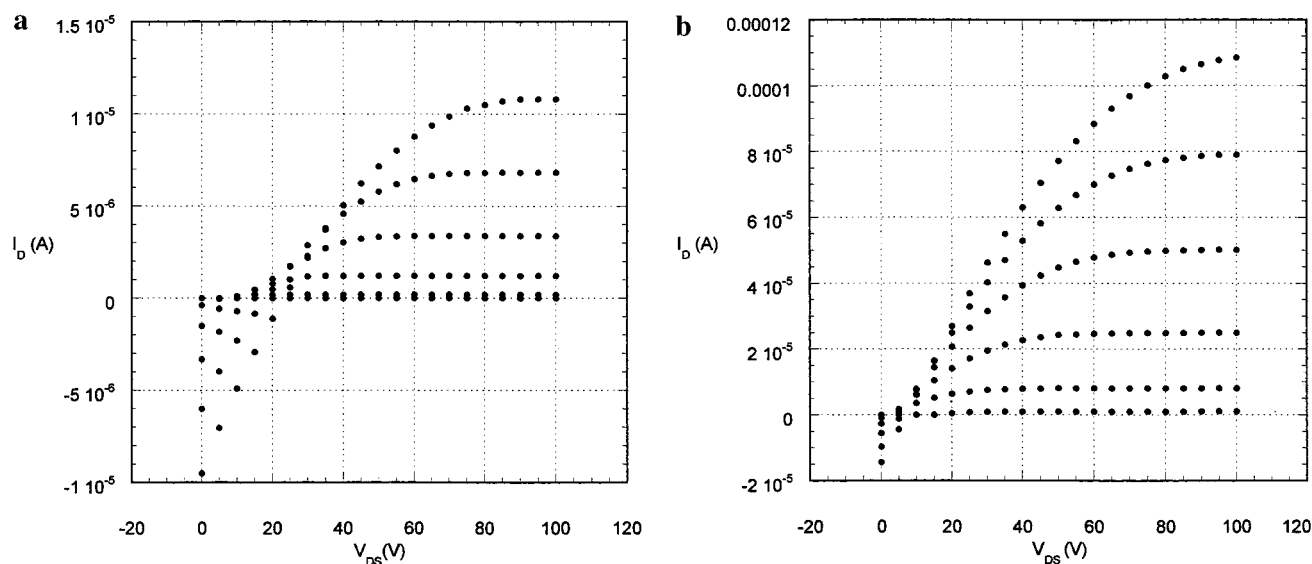


Figure 3. Current–voltage characteristics for (a) **1** vacuum deposited at 70 °C substrate temperature, width/length = 4.5, and (b) **8** vacuum deposited at 98 °C substrate temperature, width/length = 19, with gold top contacts on SiO₂/Si. Gate voltages are 0–100 V in increments of 20 V, bottom to top. The off-current is decidedly lower for **1**, while the turn-on and threshold voltages are lower for **8**.

be deposited and/or patterned before the semiconducting film is applied, it would be desirable to uncover an electrode–semiconductor combination that works reliably in the bottom contact geometry. The reproducibility of gold top contacts, especially with **8**, made gold an attractive electrode material, but transistor activity was rarely observed in the bottom contact configuration, even in side-by-side experiments where a single deposition produced high activity top-contact devices.

As discussed in the Introduction, thiol-on-gold coatings may be effective via a plurality of mechanisms, and it was not clear which of these mechanisms might be operative with the present

compounds. Therefore, a series of thiols and other commercially available sulfur reagents with a variety of terminal functional groups were initially screened using the readily available compound **2**. The data from devices made for this screening are listed in Table 3. Several of the thiol treatments provide an obvious beneficial effect, although no device produced a current as high as the top contact control.

On the basis of the data, four compounds were selected for further testing with other semiconductors: three substituted benzyl mercaptans and the carboxylic acid. Bottom contact currents were negligible with compounds **3–5** and **7**. However,

Table 3. Currents for 100 V Drain and Gate Applied to Reagent-Treated Bottom Contact Gold FETs with **2** Deposited on SiO₂/Si with W/L = 17

reagent	functional group	deposition temp for 2	current (nA)
none		ambient	<20
6-hydroxy-1-hexanethiol	OH	ambient	40
2-chlorobenzyl mercaptan	2-ClC ₆ H ₄	ambient	500–1300
3-mercaptopropanoic acid	COOH	ambient	1400
none		55 °C	<10
benzyl mercaptan	C ₆ H ₅	55 °C	100
2-chlorobenzyl mercaptan	2-ClC ₆ H ₄	55 °C	100–400
4-chlorobenzyl mercaptan	4-ClC ₆ H ₄	55 °C	200
4-methoxybenzyl mercaptan	4-MeOC ₆ H ₄	55 °C	500–1300
methyl 3-mercaptopropanoate	COOMe	55 °C	10–50
3-mercaptopropanoic acid	COOH	55 °C	20–60
2-naphthalenethiol	SH	55 °C	5
sulfur	SS	55 °C	1
tetrathiafulvalene		ambient	0
top contact		ambient	3000

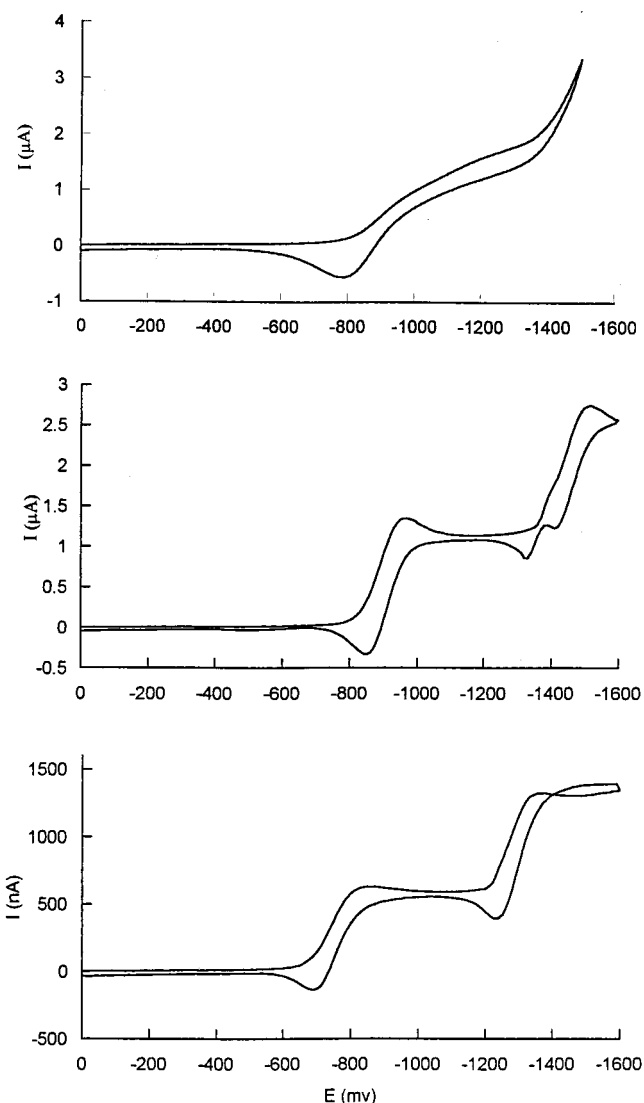
Table 4. 100-V Currents for Thiol-on-Gold Bottom Contact FETs with **1**, **6**, and **8** (same configuration as in Table 3)

semiconductor	thiol	deposition temp	current (μA)
1	2-chlorobenzyl mercaptan	50 °C	6
	4-methoxybenzyl mercaptan	50 °C	4
	4-chlorobenzyl mercaptan	50 °C	7–13
	3-mercaptopropanoic acid	50 °C	6
	top contact	50 °C	8 ^a
	2-chlorobenzyl mercaptan	70 °C	7
	4-methoxybenzyl mercaptan	70 °C	5
	4-chlorobenzyl mercaptan	70 °C	5
	3-mercaptopropanoic acid	70 °C	0.4
	none	70 °C	<0.05
6	top contact	70 °C	7 ^a
	2-chlorobenzyl mercaptan	50 °C	0.12
	4-methoxybenzyl mercaptan	50 °C	0.25
	4-chlorobenzyl mercaptan	50 °C	0.1
	3-mercaptopropanoic acid	50 °C	0.2
	none	50 °C	0
8	top contact	50 °C	0.02
	2-chlorobenzyl mercaptan	50 °C	3
	4-methoxybenzyl mercaptan	50 °C	3
	4-chlorobenzyl mercaptan	50 °C	8
	3-mercaptopropanoic acid	50 °C	0.4 ^b
	none	50 °C	0.4 ^b
	top contact	50 °C	8
	2-chlorobenzyl mercaptan	70 °C	50
	4-methoxybenzyl mercaptan	70 °C	2
	4-chlorobenzyl mercaptan	70 °C	5
none	70 °C	0.3 ^b	
top contact	70 °C	35	

^a May have been barrier limited because of the use of thin electrodes.

^b Very large scatter.

substantial currents were observed with compounds **1**, **6**, and **8**, and are listed in Table 4. The general trend is that thiol-treated devices produced much higher currents than do bottom contact controls. The highest currents were obtained with **8**, with some bottom contact device currents exceeding those of the top contact controls. The promising results with **8** prompted an extended study of **8** using higher deposition temperatures. To ensure that the thiol coatings would not desorb under extensive pumpdown at these temperatures, the higher-boiling thiol 3,4-dichlorobenzyl mercaptan was synthesized and used to treat bottom-contact substrates. At a deposition temperature of 90–100 °C, maximum currents exceeding 100 μA were observed equivalently from thiol-coated bottom contact and top contact control devices, corresponding to apparent mobilities of ca. 0.1 cm²/(V s). This thiol also increased the current output

**Figure 4.** Cyclic voltammograms for **1** (bottom), **3** (middle), and **8** (top).

of a bottom contact PFCP device fabricated by evaporation of the semiconductor at 125 °C by a factor of 50. The 4-chlorobenzyl mercaptan increased a room-temperature-deposited PFCP device on-current by a similar factor, and 2-chlorobenzyl mercaptan treatment increased the “apparent” mobility of a bottom contact device made from solution deposited **1**¹⁶ by a factor of 50. The dichlorobenzyl mercaptan could be applied by printing with a silicone stamp onto a gold film, followed by etching the uncoated regions of the gold with a standard aqueous ferrocyanide–ferricyanide solution. XPS showed thiol remaining on the unetched gold.

To gauge the relative roles of orbital energy and conformational/packing effects in determining mobility and air stability, comparative reduction potentials of compounds **1**, **3**, and **8** were determined. Cyclic voltammograms are illustrated in Figure 4. The first redox process was observed at -0.77 , -0.91 , and -0.9 V, respectively, versus nonaqueous Ag/AgNO₃. The ferrocene redox couple was found at 0.15–0.20 under the same conditions.

Preliminary data indicate that **1** packs in a herringbone manner as a solution-grown single crystal, while **8** forms a stacked single-crystal polymorph from solution that is not commensurate with the thin film packing. However, the single-crystal mobility of **8** in at least one direction is considerable. Detailed crystal

structure analyses and single-crystal electronic properties will be published separately.²²

Discussion

The striking differences in mobility under ambient atmosphere between the fluorinated compounds **1**, **2**, and **8** on one hand and nonfluorinated analogues **3–5** and **9** on the other can be explained by at least three possible effects. The fluorinated substituents could impart sufficient additional electron-withdrawing character to the conjugated cores to stabilize injected electrons against environmental traps. The substituents could also provide screening against penetration of environmental contaminants into the channel region of an active film in an FET. Finally, the side groups could induce a more favorable packing geometry that increases intermolecular overlap and/or reduces phonon scattering. To a certain extent, these effects must also influence threshold voltages and on/off ratios.

The electron-withdrawing effect would be expected to be minor, and based on the electrochemistry, actually is. Although there may be some uncertainty about the exact reduction voltages because of possible aggregation effects,²³ especially with **8**, it is clear that none of the reduction potentials are less negative than that of NTCDA²⁴ or C₆₀,²⁵ which themselves are not operable in air. The potentials measured are formally outside the “stability window” for n-channel materials defined by de Leeuw.²⁶ The electrochemical differences among the three compounds examined appear barely significant. Additionally, the moderate activity of compound **6** as an FET film in air is further evidence against the electron-withdrawing nature of the substituent as a dominant effect.

Therefore, solid-state packing effects must be of vital importance in explaining the behavior of the NTCDI semiconductors. One might imagine that the side chains of **1** occupy a larger volume fraction of a crystal than would the chains of **3** packed in an analogous orientation, and therefore would be more effective at barring the penetration of water and oxygen into the interior of a film. However, it is difficult to argue that the CF₃ group of **8** would be so much more sterically blocking than the CH₃ of **9**. It is even less obvious why the on/off ratios of **1** and **8** would be so different. Crystallographic studies of all four compounds are in progress in an attempt to resolve these issues. Nevertheless, it is likely that a combination of all of the factors discussed in this section will prove to be relevant.

The fact that thiols with varied polarities and dipole directions but common possibilities for intermolecular interactions with NTCDI are effective suggests that the thiols' effectiveness is due to a physisorption phenomenon. Examples of such beneficial surface effects include increased wetting or sticking of the

NTCDI (or PFCP) as it is deposited on the thiol-treated gold versus bare gold, or decreased tendency to delaminate after deposition or during device operation. Favorable aryl–aryl interactions or COOH–carbonyl hydrogen bonds are probably responsible for these effects, and such effects need to be optimized for specific semiconductors. On the other hand, the direction of the surface dipole or degree of charge redistribution induced by the thiol are not likely to be very important in this situation, though they are thought to be important in organic light-emitting device interfaces.²⁷ The reactivity of the electrode surfaces as the NTCDI is deposited should be negligible, in contrast to the situation where metals are deposited onto organics, or where dopants are deliberately introduced near the metal–organic interface. The drastically different effects of the thiols at various temperatures could be due to thermally induced dimerization (such as COOH groups forming anhydrides), desorption, or reorientation that occurs for different thiols at different temperatures.

Conclusion

The higher mobility compounds discussed in this paper should be useful in devices and circuits that require electron transporting semiconductors and are to be fabricated with rapid sublimation or solution deposition techniques. The mobility demonstrated for **8** would provide a 3- to 4-fold enhancement in the speed of a complementary circuit when substituted for PFCP. On the other hand, a similar enhancement in power efficiency could be obtained by taking advantage of the higher on/off ratio of **1** and **2**. Improved performance of photorefractive media and solar cells is conceivable from the incorporation of continuous domains of the better NTCDI derivatives. A related compound, *N,N'*-bis(1,2-dimethylpropyl)-1,4,5,8-naphthalenetetracarboxylic diimide, in a polystyrene composite, has displayed an electron mobility of ca. 10⁻⁵ cm²/(V s).²⁸ Such composites are of interest as xerographic photoreceptors, and may also be improved through the use of compounds and molecular assemblies described here.

In summary, two exemplary compounds were identified for n-channel FET semiconductors, one optimized for on/off ratio and the other for mobility. A means of using them on bottom-contact gold electrodes was devised involving specific thiol coatings on the gold surfaces. The application of these findings to the fabrication of more complex circuits is in progress.

Acknowledgment. I am indebted to Dr. Z. Bao for deposition of PFCP films and Dr. Y.-Y. Lin for testing and providing the substrate for the thiol-treated device with solution-deposited **1**. I also thank Drs. R. Zehner, A. Dodabalapur, P. Littlewood, and Z. Bao for valuable discussions and advice.

JA000870G

(22) Katz, H. E.; Siegrist, T.; Schön, J. H.; Kloc, Ch.; Batlogg, B.; Lovinger, A. J.; Johnson, J. Submitted for publication.

(23) Penneau, J.-F.; Stallman, B. J.; Kasai, P. H.; Miller, L. L. *Chem. Mater.* **1991**, *3*, 791. Müller, L. L.; Mann, K. R. *Acc. Chem. Res.* **1996**, *29*, 417.

(24) De Luca, C.; Giomini, C.; Rampazzo, L. *J. Electroanal. Chem.* **1990**, *280*, 145.

(25) Allemand, P. M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050.

(26) De Leeuw, D. M.; Simenon, M. M. J.; Brown, A. R.; Einerhand, R. E. F. *Synth. Met.* **1997**, *87*, 53.

(27) Schlaf, R.; Merritt, C. D.; Crisafulli, L. A.; Kafafi, Z. H. *J. Appl. Phys.* **1999**, *86*, 5678.

(28) Borsenberger, P. M.; Gruenbaum, W. T.; Magin, E. H.; Visser, S. A.; Schildkraut, D. E. *J. Imaging Sci. Technol.* **1999**, *43*, 201. Borsenberger, P. M.; Gruenbaum, W. T.; Magin, E. H.; Visser, S. A.; Schildkraut, D. E. *Phys. Stat. Sol. A* **1998**, *166*, 835.