*J. Am. Chem. Soc.* **1996,** *118,* 11331−11332 11331

# n-Channel Organic Transistor Materials Based on Naphthalene Frameworks

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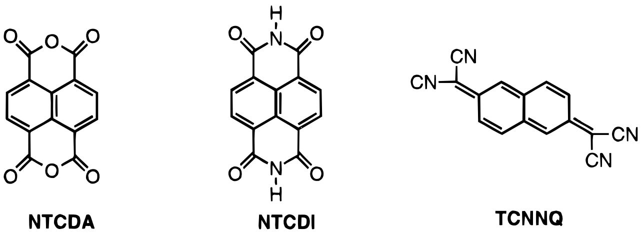
*Received July 17, 1996*

There has been recent rapid progress in the synthesis of organic semiconducting materials for field effect transistors (FETs) useful for plastic electronics. Most of the high-mobility compounds have been mainly hole transporters with mobilities ranging from 0.01 to 0.6 cm$^2$ V$^{-1}$ s$^{-1}$.[1−4] For applications such as complementary circuits,[5] a combination of n- and p-channel FETs is required, necessitating the concurrent development of organic n-channel FETs. Organic FETs based on $C_{60}$ have been reported which exhibited high electron-transporting (n-type) mobilities.[6,7] However, devices utilizing this compound are highly oxygen-sensitive and thus may not be suitable for practical applications. Evidence of n-type conduction was also reported for organic FETs fabricated from perylene tetracarboxylic dianhydride (PTCDA),[8] *N*,*N′*-diphenyl-3,4,9,10-perylene tetracarboxylic diimide (DP-PTCDI),[9] intentionally-doped tetracyanoquinodimethane (TCNQ),[10] and rare-earth bisphthalocyanines under certain conditions.[11] For all these materials, the highest mobility achieved is on the order of 10$^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$.

1,4,5,8-Naphthalene tetracarboxylic dianhydride (NTCDA), which has been previously used in organic heterostructures,[12] has the naphthalene framework, which can potentially lead to a high mobility.[13] Although NTCDA is much less extensively conjugated compared to the n-type perylene compounds and its crystal structure indicates only partial intermolecular overlap, it has an accesible LUMO for electron injection.[14,15] Here we report electron[16] mobilities up to 3 × 10$^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ for compounds based on NTCDA (Chart 1) as well as preliminary indications of similar mobilities in 11,11,12,12-tetracyanonaphtho-2,6-quinodimethane (TCNNQ), which also has the naphthalene framework and is easily reduced.[17]

**Chart 1**



NTCDA, NTCDI, and TCNNQ were purchased from Aldrich, ICN, and TCI Chemical Co., respectively, and were purified by vacuum sublimation using pressures of 10$^{-4}$ Torr or lower. The FETs were fabricated using thermally grown silicon dioxide (300 nm) as the insulating layer on n-type silicon, which acts as the gate electrode. Gold source and drain contacts were photolithographically defined to give channel width $W = 250$ $\mu$m and channel lengths $L = 4$, 12, and 25 $\mu$m. The semiconductor was then vacuum-deposited onto the substrates at base pressures of 3 × 10$^{-6}$ Torr or lower to make thin films with thicknesses of ca. 500 Å. The electrical characteristics of the FETs were measured under vacuum using a Hewlett-Packard 4145b semiconductor parameter analyzer.

Figure 1 shows the electrical characteristics of an FET fabricated from NTCDA deposited at a substrate temperature of 55 °C for a 12 $\mu$m channel length device. The curve shows a linear regime at low drain-source voltages and a saturation regime at higher drain-source voltages. Evidence of n-type conduction is present since positive gate biases are required to achieve increasing drain-source currents under positive drain voltages. The field effect mobilities $\mu_{FET}$ were calculated in the saturation regime using the equation[18]

$$I_{DS} = \frac{WC_i}{2L}\mu(V_G - V_o)^2 \tag{1}$$

where $L$ and $W$ are the channel length and width, respectively, $C_i$ is the capacitance per unit area of the oxide, and $V_o$ is the extrapolated threshold voltage. The latter can be calculated from a plot of $I_{DS}^{1/2}$ vs $V_G$. Field effect mobilities of (1−3) × 10$^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ were obtained for NTCDA-based FETs deposited at a substrate temperature of 55 °C. These mobilities are the highest achieved so far for any n-type organic semiconductor with the exception of $C_{60}$. The high mobilities were observed when the device was operated under vacuum. In air, however, a 1−2 order of magnitude decrease in the electron mobilities was noted. Similarly, diminished mobilities were also observed when the devices were exposed to atmospheric moisture after evaporating the semiconductor. Currents scale inversely with channel lengths, as expected. Similar calculations were done for FETs prepared at ambient temperature. For devices deposited at $T_{sub} = 25$ °C, a $\mu_{FET}$ on the order of 10$^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ was achieved, an order of magnitude lower compared to the higher substrate temperature. The difference in the mobilities observed using the different substrate temperatures could possibly be due to changes in the morphology at elevated temperatures. Although electron micrographs show similar average grain sizes (ca. 200 nm) for films deposited at both substrate temperatures, the film deposited at the higher temperature may be more continuous or better ordered in the channel region. Alternatively, we can hypothesize that the interfacial bonding between the dielectric and semiconductor may be improved or tiny amounts of impurities may be selectively desorbed from the semiconductor at the higher temperature. We have ruled out desorption of any preadsorbed impurities from the substrate by X-ray photoelectron spectros-

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S0002-7863(96)02461-4 CCC: $12.00

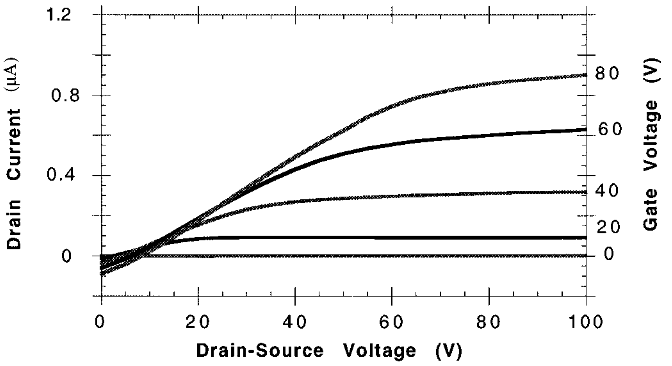

**Figure 1.** $I_{DS}$ vs $V_{DS}$ characteristic of a typical NTCDA FET prepared at $T_{sub} = 55$ °C, with channel length = 12 $\mu$m and channel width = 250 $\mu$m.

copy (XPS) studies. A similar sensitivity of mobility to temperature has been observed in p-type compounds.[2,19,20]

FETs were also fabricated using 1,4,5,8-naphthalene tetracarboxylic diimide (NTCDI) as the semiconducting layer. For these devices, $\mu_{FET}$ values on the order of $10^{-4}$ were obtained, an order of magnitude lower than NTCDA. A similar trend was also observed for PTCDI relative to the already low mobility of PTCDA.

For PTCDA and presumably its imide derivative as well, the low mobility may be attributed to the modest overlap between molecules in the direction of the current flow in the transistor geometry.[8] On the other hand, NTCDA packs in a herringbone pattern which, while not perfectly stacked, allows for intermolecular interactions along all three axes.[14] X-ray diffraction results of films prepared simultaneously with the transistors show NTCDA molecules stand close to perpendicular to the substrate with the herringbone trace along the substrate. Thus, the electron flow is most likely in a direction with an edge to face overlap, as is the case for holes in α-6T.[21]

Preliminary work on TCNNQ FETs has indicated electron mobilities higher than TCNQ without intentional doping and comparable to NTCDA but with greater stability in air. The high off-current observed for this material may be due in part to adventitious dopants and thus could still be a contributing factor to the measured mobility. However, considerable dedoping was accomplished by treatment with iodine vapor with little loss of mobility. In TCNQ, substantial doping levels were required to achieve a maximum $\mu_{FET}$ of $3 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$.[10]

In conclusion, we have shown that n-type mobilities above $10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ are achievable in readily available organic compounds. This provides an avenue by which all-organic complementary circuits can be realized. Such circuits could be fabricated from separate n- and p-channel transistors or through the use of novel heterostructure transistors. Current work is directed to the enhancement of the mobility and environmental stability of the n-channel devices.

**Acknowledgment.** The authors are grateful to R. Opila and H. Krautter for surface analyses. We also thank Z. Bao, L. J. Rothberg, E. Reichmanis, and R. E. Slusher for fruitful discussions.

JA962461J

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