Unsymmetrical n-Channel Semiconducting Naphthalenetetracarboxylic Diimides Assembled via Hydrogen Bonds

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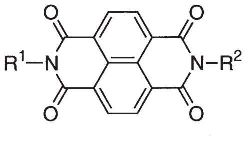
Organic field-effect transistors have been fabricated from novel naphthalenetetracarboxylic diimides with unsymmetrical substitution. Two of these show distinct electron mobility, providing the first evidence that hydrogen bonding can be a means of producing a semiconducting morphology from organic compounds.

Organic molecular solids are of interest as semiconductors in field-effect transistors (FETs) and other devices.[1] Functional circuits containing up to hundreds of organic semiconductor FETs have been fabricated.[2–4] Additional responses such as chemical sensitivity[5] and nonvolatile memory[6] can be utilized. Most organic semiconductors are members of a few broad classes of compounds: conjugated oligomers; fused ring compounds; and regioregular polythiophenes, although organic–inorganic hybrid semiconductors have also been incorporated into FETs.[7]

The substituent pattern on all of the discrete organic semiconducting compounds reported so far is at least two-fold symmetric, including a series of naphthalenetetracarboxylic diimides (NTCDIs)[8,9] that display the rare capability of n-channel activity in thin film FETs.[10–12] Furthermore, there are no particular interlayer interactions among molecules in typical organic semiconducting solids. In this letter, we describe novel NTCDIs with unsymmetrical substitution. Two of these show distinct electron mobility in FETs. More importantly, they provide the first evidence that weak bond assembly can be a means of producing a semiconducting morphology from organic compounds. In addition, the data corroborate and generalize observations we[13] and others[14] have previously made with symmetrical compounds concerning the effect of fluorinated and nonfluorinated substituents on n-channel activity.

Compounds **1**–**3**, which are shiny gold in color, and their model compounds **4** and **5** were synthesized using a modification of a previously described method.[15] The structures were fully characterized with ^{1}H NMR, MS, and elemental analyses.



	R^1	R^2
1	$CH_3(CH_2)_7$	NH_2
2	$CF_3(CF_2)_6CH_2$	NH_2
3	$CF_3(CF_2)_2CH_2$	NH_2
4	$CH_3(CH_2)_7$	$N(CH_3)_2$
5	$CH_3(CH_2)_7$	$(CH_2)_7CH_3$

Sublimed films of **1** on standard room temperature doped Si/SiO$_2$ test vehicles (300 nm oxide thickness, common gate) followed by vapor deposition of gold source and drain electrodes (channel width 4 mm, channel length 0.2 mm) gave FETs showing n-channel mobility $<10^{-5}$ cm^2/V s in air, near the minimum measurable mobility. However, measurement under vacuum after pumping on the sample for several days gave a more substantial mobility of 3×10^{-4} cm^2/V s. The activity was completely quenched on readmission of air into the apparatus. A film of **2** similarly deposited was much less active, but when deposited on a 70 °C substrate, a mobility of 5×10^{-5} was measured in air (Figure 1). The increased mobility in air brought about by fluorocarbon chain substitution parallels the effect previously seen in the higher-mobility symmetrical NTCDIs.[8] This is not simply a general effect of heating; when **1** was deposited on a 70 °C substrate, the mobility in air was negligible, and rose above 10^{-5} cm^2/V s only on pumping for a week. The mobility of **2** did also increase further on extended pumping, to 2×10^{-4} cm^2/V s. The extended time needed for pumping operations indicates that traps are bound deep within the solid film, with a significant activation barrier to their desorption.[16] The mobility of N,N-dimethyl derivative **4**, which is uncapable of hydrogen bonding, did not rose above 10^{-5} cm^2/V s either on a room-temperature or 70 °C substrate even under vacuum. Compound **3** was initially inactive as an FET, and on pumping, showed leakage currents but little distinguishable field-effect current.

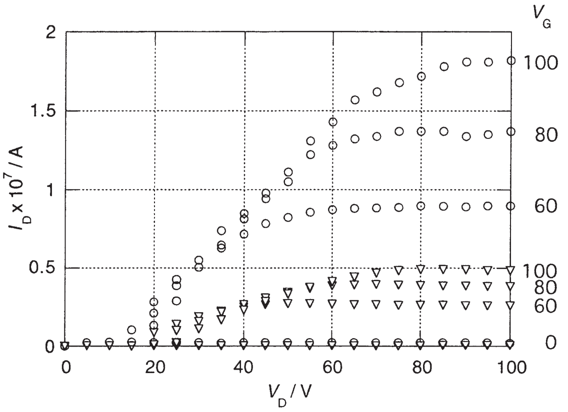


Figure 1. Drain current as a function of drain voltage for **2** at gate voltages of 0, 60, 80, and 100 V. Triangles are as measured in air, and circles are after 10-h pumping under vacuum.

The solid state structures of these materials were probed by IR and X-ray studies and the results for **1** will be given here as a representative example. The IR spectrum of a film of **1** deposited on an NaCl plate (Figure 2) includes a sharp NH stretch band at 3339 cm^{-1} and a broader feature between 3240 and 3280 cm^{-1}. N-aminophthalimide[17] and N-aminonaphthalimide,[18] whose X-ray crystal structures adopt head-to-head off-

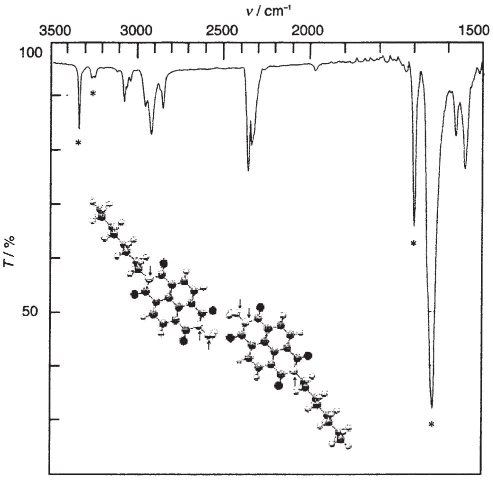


Figure 2. The IR spectrum of a film of **1**. Peaks indicated by an asterisk are mentioned in the text. The structure displayed is the B3LYP/6-31G* optimized geometry for the dimer of **1** (nitrogens are indicated by arrows).

set arrangements of the hydrogen-bonded aminoimide groups in layer pairs, have NH stretch features within 10–20 cm^{-1} of those of **1**. The carbonyl stretch bands of **1** appear at 1644 and 1699 cm^{-1}. These values are lower in wavenumber by 5–25 cm^{-1} than those of non-hydrogen bonding **4** and **5**, suggesting that the carbonyl groups in **1** are involved in hydrogen bonding.[19] Finally, the X-ray diffraction of the films of **1** shows a strongly defined layer spacing of 25 Å. This is intermediate between the single and double length of the molecule.

These observations are consistent with a structure such as that proposed in the inset of Figure 2. This structure is based on electronic structure calculations carried out with the Gaussian-98 program package. The structures of the monomer and the dimer were completely optimized using the gradient-corrected B3LYP density functional with the polarized 6-31G* basis set (B3LYP/6-31G*). Similar optimizations were also carried out at the Hartree-Fock level with the 6-31G* basis set (HF/6-31G*) but the results are very similar. The dimer is held together by two hydrogen bonds between the N–H hydrogen in one monomer and the carbonyl oxygen of the other monomer. The hydrogen bonding distance is 2.11 Å at the B3LYP/6-31G* level and 2.26 Å at the HF/6-31G* level. The two aromatic planes of the monomers are offset by about 2–3 Å so that only one of the N–H bonds in each monomer takes part in hydrogen bonding. The octyl groups at the ends of the aromatic structures were held in all-*trans* conformations in the calculations. The distance of the farthest carbons in the dimer is 36.4 Å at the B3LYP/6-31G* level, about twice the monomer end-to-end distance. However, since the octyl groups are out of the aromatic plane, much smaller layer spacings are likely. For example, for the orientation shown, the vertical distance is about 26 Å, which allows for the aromatic rings between adjacent dimers to be roughly parallel. Compound **2** showed an analogous layer spacing of 27 Å, but with less crystallinity.

Transmission electron microscopy revealed a smooth but polycrystalline morphology for **1** deposited at room temperature, but a network of poorly connected micron-length rectangular lamellae for the elevated temperature deposition. Compound **2** formed unconnected 10–50 nm grains at room temperature, and slightly larger and more three-dimensionally isotropic, somewhat connected grains at higher temperature. Thus, the mobilities, especially on the 70 °C samples, are undoubtedly not intrinsic solid state values, and may be severely limited by grain boundary barriers.[20] Compound **3** formed a completely disordered, discontinuous film, based on both X-ray diffraction and transmission electron microscopy, consistent with its lack of transistor activity.

The assumed structure of the semiconducting films made from **1** and **2** implies that, even though intergrain barriers probably prevented the realization of a mobility advantage from these particular compounds, hydrogen bonding can be helpful in the design of higher mobility organic semiconductors based on other conjugated rings, where the hydrogen bonds might induce favorable intermolecular π-system interaction. This motif might also be useful in cases where a symmetrical derivative of a ring system is harder to synthesize or less soluble than an unsymmetrical derivative, or where an intricate pattern of distinct molecules in a film might be of interest. Furthermore, hydrogen bonding could be used to impart increased and/or more specific chemical sensitivity to FET-based sensors and sensor arrays, both by providing binding sites and avenues for charge transport perturbation. Finally, the comparison of the 70 °C films of **1** and **2** provides further independent evidence of the previously observed[13,14] and incompletely explained beneficial effect of fluoroalkyl chains in stabilizing mobile electrons in organic semiconductors, especially against atmospheric quenching.

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