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Trifluoromethyltriphenodioxazine: Air-Stable and High-Performance n-Type Semiconductor

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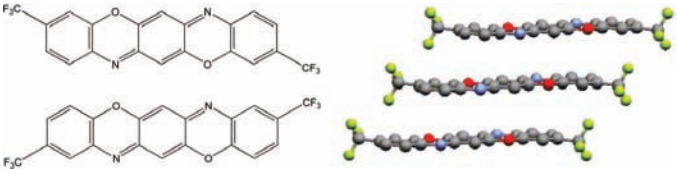
ABSTRACT



Two trifluoromethyltriphenodioxazines were efficiently synthesized as active materials for n-type organic field-effect transistors, and their optical and electrochemical properties were characterized. Air-stable and high-performance thin film transistors based on the two compounds were fabricated.

Small molecule organic semiconductors have been studied extensively as materials for light-emitting diodes, photovoltaic cells, and field-effect transistors (OFETs).[1] Among these applications, OFETs are considered attractive alternatives to conventional inorganic transistors in functions that require low-cost, low-temperature fabrication, solution-phase device processing, and mechanical flexibility.[2] The basic OFET structure includes three contacts (source, drain, and gate), a dielectric, and a semiconductor, with the latter functioning as either p-type (hole-transporter) or n-type (electron-transporter) charge carrier. p-Type organic semiconductors have been widely studied and have excellent field-effect characteristics,[3] whereas n-type materials are relatively rare,

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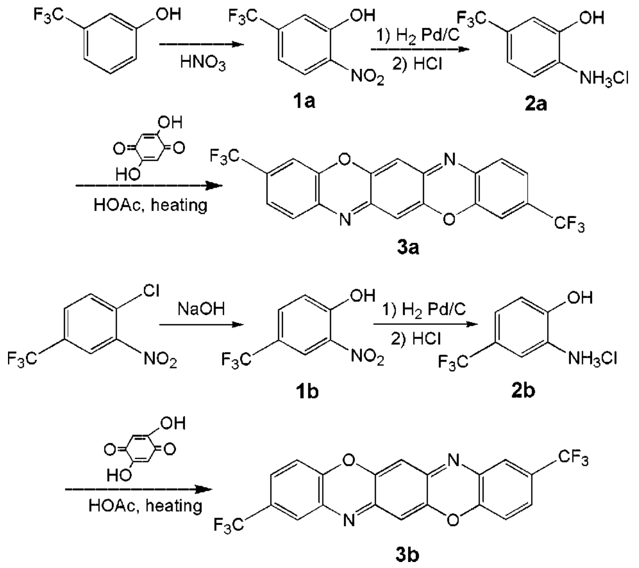
with unsatisfactory field-effect performance.[4] However, n-type semiconductors are envisioned as key components of organic p-n junction, bipolar transistors, ring oscillators, and complementary integrated circuits.[5] Therefore, the design and synthesis of novel n-type organic semiconductor materials are crucial for the development of practical organic electrics. In order to obtain high electron mobility, the organic semiconductor layer should be highly ordered with strong intermolecular interaction and should also have a proper energy level of the lowest unoccupied molecular orbital (LUMO) near the work functions of source/drain electrodes.[5] Besides, the electron affinity, which is defined as the energy difference between the LUMO and vacuum level, could influence the stability of n-type materials to a very large extent. In general, large electron affinity is necessary to obtain air-stable n-type materials. As a result, exploration of organic semiconductors with high electron affinity is an effective way to realize high performance stable n-type OFETs. As an example, introducing fluoro or fluoroalkyl substituents into pentacene and oligothiophene derivatives could lead to high electron affinity and result in high performance n-type organic semiconductors.[6] Perfluoropentacene has positively shifted redox potentials relative to those of the nonfluorinated compound and was found to adopt the same herringbone structure as pentacene.[7] In the herringbone structures, organic molecules are packed more or less edge-to-face in two dimensional layers, minimizing the π-overlap between adjacent molecules. π-Stacks in a face-to-face structure can increase the intermolecular interactions, facilitating charge transport.[8] On the other hand, planar molecules are considered to be favorable for a large transfer integral between two neighboring molecules and less reorganization energy upon ionization, which are required for high mobility.[9] Here we have designed and synthesized planar molecules with trifluoromethyl groups **3a** and **3b**, which have a planar geometry similar to that of pentacene. Molecules of **3a** self-assemble in the solid state to give efficient intermolecular interactions in all three dimensions. The OFETs based on compounds **3a** and **3b** were air-stable and showed excellent n-type device performance.

Scheme 1. Synthesis of Compounds **3a** and **3b**



The synthetic routes to the novel n-type transport materials are shown in Scheme 1. 3-Hydroxybenzotrifluoride was nitrified to give 2-nitro-5-trifluoromethylphenol (**1a**). 2-Nitro-4-trifluoromethylphenol (**1b**) was prepared by the reaction of sodium hydroxide with 2-nitro-4-trifluoromethylchlorobenzene in dimethyl sulfoxide. Pd/C-catalyzed reduction reaction of the nitrophenols **1a** and **1b** was carried out in a H_2 atmosphere followed by treating with dry HCl gas, to give the 2-amino-5-trifluoromethylphenol hydrochloride (**2a**) and 2-amino-4-trifluoromethylphenol one (**2b**), respectively. The obtained 2-aminophenol hydrochlorides **2a** and **2b** were treated with 2,5-dihydroxy-[1,4]benzoquinone in the presence of acetic acid, to give the 3,10-ditrifluoromethyl-triphenodioxazine (**3a**) in 94% yield and 2,9-ditrifluoromethyl-triphenodioxazine (**3b**) with a yield of 67%. The compounds **3a** and **3b** were purified by sublimation, and their molecular structures were determined by spectral data along with elemental analysis.

A crystal of **3a** suitable for single-crystal X-ray diffraction studies was grown in a physical vapor growth process. The crystal structure is based on π-stacking along the *a*-axis direction in which the plane-to-plane is ca. 3.44 Å. The close face-to-face $\pi-\pi$ stacking lies in the direction normal to the molecular plane. Pentacene crystallizes into a herringbone arrangement with no intermolecular cofacial interactions.[10]

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The close face-to-face $\pi-\pi$ interactions could give rise to efficient charge carrier transport.

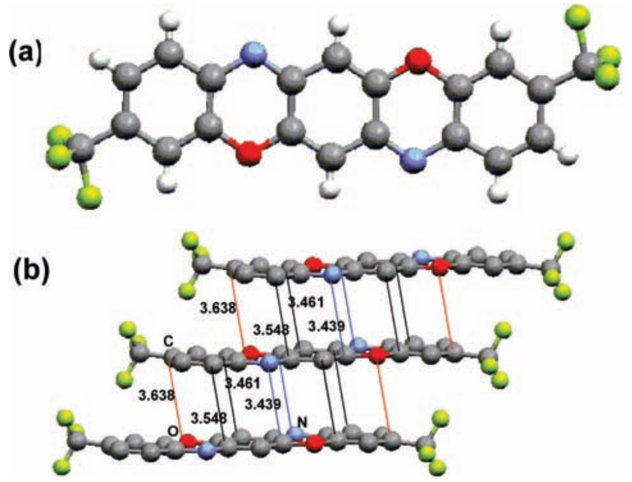

Figure 1. (a) Crystal structure of **3a**. (b) Face-to-face $\pi-\pi$ stacking.

The XRD pattern of a thin film of **3a** prepared by vacuum evaporation exhibits three strong diffraction peaks, which are attributed to the (0,0,1), (0,0,2), and (0,0,4) planes assigned from the diffraction pattern calculated from the single-crystal XRD data (Figure S1, Supporting Information). The thin film is highly crystalline. The thin films of **3b** show diffraction peaks similar to those of **3a**. This result indicates that the **3a** or **3b** molecules pack into high orientation thin films.

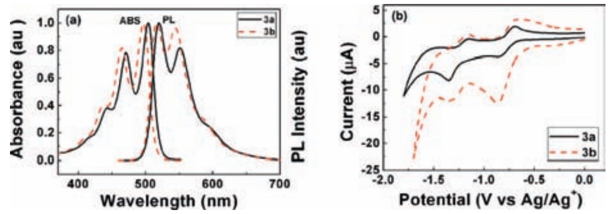

Figure 2. (a) Absorption and PL spectra of compounds **3a** and **3b** in CH_2Cl_2. (b) Cyclic voltammograms of compounds **3a** and **3b** in CH_2Cl_2..

Absorption and photoluminescent spectra of compounds **3a** and **3b** in CH_2Cl_2 are shown in Figure 2. The compound **3a** exhibits three absorption peaks at 442, 470, and 504 nm and two PL maxima at 520 and 550 nm. The absorption and PL spectra of the compound **3b** are similar to those of the compound **3a**, with a slight blue shift of 4−6 nm. The compounds **3a** and **3b** exhibit a similar electrochemical behavior, which is not affected by position of the trifluoromethyl groups. Two reversible anodic redox couples with half-wave potentials of −0.77 and −1.26 eV were obtained for the two compounds. The two compounds show almost the same LUMO energy levels of about −3.67 eV, which were estimated according to the equation $E_{\mathrm{LUMO}} = -(E^{1/2}_{\mathrm{red-1}} + 4.44)$ eV.[11] The HOMO energy levels for the compounds **3a** and **3b** were determined to be −6.04 and −6.06 eV, respectively, by combining the LUMO energy levels together with the band gaps obtained from the absorption edge (2.37 and 2.39 eV).

Top-contact OFETs were fabricated by vapor deposition of the compound **3a** or **3b** on octyltrichlorosilane (OTS)-treated n-Si/SiO_2 (450 nm) substrates. All devices fabricated under different substrate temperatures showed typical n-channel FET characteristics with field-effect mobility (μ_{FET}) higher than 10^{-3} cm^2 V^{-1} s^{-1} and $I_{\mathrm{on}}/I_{\mathrm{off}} > 10^4$ under ambient conditions (Table 1 and Figure 3). The excellent field-effect properties were observed in both the **3a**- and **3b**-based devices fabricated at the substrate temperature of 60 °C. The best OFETs based on **3a** and **3b** showed a mobility of 0.07 and 0.03 cm^2 V^{-1} s^{-1}, respectively. Meanwhile, these devices exhibited outstanding environmental stability. After the devices were stored under an ambient condition for 30 days, the OFETs based on compound **3a** retained high mobility (from 0.05 to 0.047 cm^2 V^{-1} s^{-1}), while the mobility of **3b** only varied from 0.02 to 0.017 cm^2 V^{-1} s^{-1}. Generally speaking, a large electron affinity is required for air-stable n-type operation. However, the electron affinity of these two compounds is about 3.67 eV, which is lower than the ones of previous reported stable n-type materials.[12] In agreement with previous reports, we suggest the close crystal packing resulting from the introduction of -CF_3 could prevent O_2 intrusion and could be responsible for high stability of these devices.[13] Therefore, molecular packing distance is another factor that might influence the stability of n-type organic semiconductors.

Table 1. FET Characteristics of **3a**- and **3b**-Based Devices Fabricated on OTS-Treated Si/SiO_2 Substrates under Different Substrate Temperatures (T_{sub})

	T_{sub} (°C)	μ_{FET} (cm^2 V^{-1} s^{-1})	$I_{\mathrm{on}}/I_{\mathrm{off}}$	V_{th} (V)
	30	0.004	10^5	31
	60	0.07	10^6	60
	80	0.04	10^7	65
3a	100	0.006	10^4	54
	30	0.003	10^5	42
	60	0.03	10^6	58
3b	80	0.01	10^6	75

In summary, we have successfully designed and synthesized a new family of n-type organic semiconductors. X-ray diffraction data of **3a** indicate that strong cofacial $\pi-\pi$

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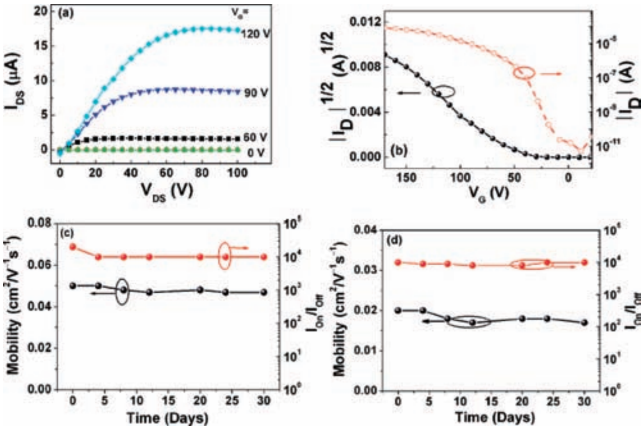

Figure 3. (a) Output and (b) transfer characteristics of the **3a**-based OFET fabricated under substrate temperature of 80 °C. Environmental stability of the OFETs based on (c) **3a** and (d) **3b**.

stacking exists between two neighboring molecules. These intermolecular interactions are helpful to the charge carrier transport. OFET devices based on the materials **3a** and **3b** showed good n-type performance with high carrier mobility and excellent device stability.

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Supporting Information Available: Experimental details for the synthesis and characterization of the compounds **3a** and **3b**, crystallographic information files (CIF) for **3a**, device fabrication, and field-effect characteristics of the devices. This material is available free of charge via the Internet at http://pubs.acs.org.

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