

1-Imino Nitroxide Pyrene for High Performance Organic Field-Effect Transistors with Low Operating Voltage

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In recent years, organic field-effect transistors (OFETs), the critical components of future organic electronics, are of great interest as a low-cost alternative to conventional silicon transistors for electronic applications.¹ Great progresses have been achieved by using superior semiconductors, and the high field-effect mobility of OFETs has been improved to more than $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with large on/off ratio for pentacene FETs, which can be comparative with the hydrogenated amorphous silicon ($\alpha\text{-Si:H}$).² Nevertheless, higher performance OFETs are still desired for practical application. Two methods have been used to improve the key OFET performance parameters, including carrier mobility, on/off ratio, and threshold voltage. One is the improvement of new device fabrication technologies, and another is the development of new organic semiconductors. Design of new organic semiconductors, one of the most challenging tasks in OFET development today, is promising by virtue of the fact that versatile molecular system have been found, involving substituted pentacenes,³ oligoselenophenes,⁴ oligothiolenylenevinylenes,⁵ thienylene-phenylene cooligomers,⁶ anthracene oligomers,⁷ pentathienoacene,⁸ and peripherally substituted indolo[3,2-*b*]carbazoles.⁹

Organic radicals are usually paramagnetic molecules and have one or more unpaired electrons, each one bringing an $S = 1/2$ spin to the molecule. They have been intensively investigated in the field of organic conductors, semiconductors and superconductors, and molecular magnetic materials. They have great potential applications in organic electronic devices, especially organic thin-film devices, due to several advantages, including the following. (1) They can form better organic film by many methods, such as high-vacuum evaporation and the Langmuir-Blodgett method. (2) They may be useful as the active layer of sensors for their sensitivity of various species. (3) Because they may show interesting magnetic properties in the solid state, multifunctional devices may be accessible. Noro et al. have utilized a transition metal complex with radical *o*-semiquinonate ligands as a semiconductor layer and successfully fabricated metal-organic thin-film transistors.¹⁰ Therefore, organic radicals will be a new class of semiconductors for OFETs. However, the OFETs utilizing an organic radical as a semiconducting layer are scarcely reported yet. Herein, we report OFETs with 1-imino nitroxide pyrene as the semiconductor layer, and the device can be operated within low voltage and shows excellent *p*-type FET characteristics.

The structure of the 1-imino nitroxide pyrene is outlined in the inset of Figure 1, and the synthesis of the 1-imino nitroxide pyrene was prepared according to the literature.¹¹ In view of the relevance of the intermolecular arrangement, pertinent to the transporting behavior and the magnetic property, magnetic susceptibility measurement of 1-imino nitroxide pyrene was performed in the temperature range of 2.0–300 K. Figure 1 shows the plot of $1/\chi$ versus temperature. The susceptibility reasonably follows a Curie–

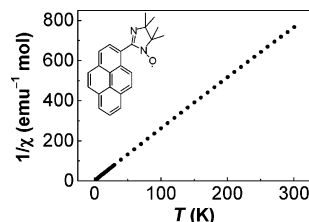


Figure 1. Chemical structure of 1-imino nitroxide pyrene (inset) and the thermal behavior of $1/\chi$ for 1-imino nitroxide pyrene.

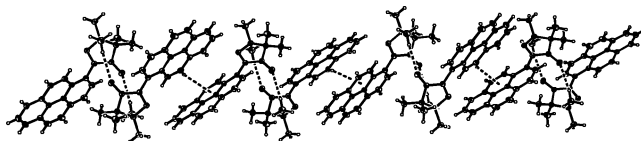


Figure 2. The 1D supermolecular chains of 1-imino nitroxide pyrene assembled by $\text{C-H}\cdots\pi$ interactions between the dimers.

Weiss law, the best fit giving a Curie constant $C = 0.390 \text{ emu K mol}^{-1}$ and a Weiss constant $\theta = -0.78 \text{ K}$, indicating the intermolecular antiferromagnetic interactions and head-to-head arrangement of molecules. The measured value of the Curie constant $C = 0.390 \text{ emu K mol}^{-1}$ is in good agreement with the expected value of $0.375 \text{ emu K mol}^{-1}$ for an $S = 1/2$ organic radical. To know the effect of the sublimation on the unpaired electrons of molecules, the ESR characterization of 1-imino nitroxide pyrene in powder form and in film form on a SiO_2/Si substrate was taken at room temperature. The ESR curves consist of a broad single line, without hyperfine splitting. The *g* value in powder form is 2.00748, consistent with that in film form. This result indicates that sublimation does not wreak havoc with the unpaired electrons of them.

A single crystal of 1-imino nitroxide pyrene was obtained by slow evaporation of solvent from dichloromethane solution. The molecule shows an asymmetric molecule geometry. The π system of the pyrene unit is planar. The five-membered ring of 1-imino nitroxide pyrene, which contains four methyl groups and one N–O (1.267 Å) free radical, is nearly coplanar with the mean and maximum deviations of about 0.11 and 0.15 Å, respectively. The pyrene unit and the five-membered ring are jointed by the C–C (1.470 Å) bond. The dihedral angle of the pyrene unit and the five-membered ring is about 38° . Moreover, two molecules form a dimer through the weak N–O \cdots H (3.5 Å, 168°) hydrogen bonds, and the pyrene units and the five-membered rings in a dimer are nearly parallel, respectively. The dimers were assembled into 1D supermolecular chains by $\text{C-H}\cdots\pi$ interactions (Figure 2).

The UV–vis spectrum of 1-imino nitroxide pyrene in dichloromethane exhibits three main absorption peaks centered at 244, 278, and 345 nm. The spectra absorptions of vacuum-deposited

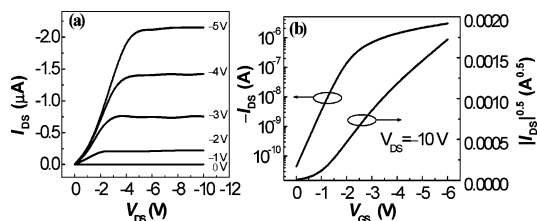


Figure 3. FET characteristics of an OFET with vacuum-deposited 1-imino nitroxide pyrene on a SiO₂/Si substrate: (a) output characteristic of the OFET device and (b) transfer characteristic of the OFET device.

thin films, resembling that obtained in solution, show slightly bathochromic shifts, with absorption peaks centered at 245, 281, and 349 nm. The optical band gap obtained from the absorption edge is 3.1 eV. The electrochemical stability of the compound was examined by cyclic voltammetry. It showed one oxidation peak and one reduction peak (an onset oxidation potential at 0.74 eV vs Ag/Ag⁺), corresponding to an estimated HOMO of -5.45 eV and the HOMO–LUMO energy gap of 2.93 eV, which is consistent with the result obtained from the UV–vis spectra measurement.

OFETs were constructed on a SiO₂/Si substrate with top-contact configuration (for details of fabrication and characterization of OFET devices, see Supporting Information). The transistor responses were observed only for negative gate bias, which means that 1-imino nitroxide pyrene is a *p*-type semiconductor. The output and transfer characteristics of a typical OFET deposited on a SiO₂/Si substrate are shown in Figure 3. The OFETs based on 1-imino nitroxide pyrene exhibited good FET behaviors, and the current–voltage characteristics conform well to the conventional transistor models in both linear and saturated regimes. The devices afforded a hole mobility of about $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with an on/off ratio of nearly 5×10^4 , much larger than those of the pyrene derivatives¹² and transition metal complex with radical *o*-semiquinonate ligands.¹⁰ This is the OFET with the highest performance for the examples of OFETs based on an organic radical. Most remarkable feature of the OFETs is the low threshold voltage (about -0.6 V) and inverse subthreshold slope (about $540 \text{ mV decade}^{-1}$), which are much lower than those of OFETs based on many organic semiconductors with SiO₂ as the gate insulator, such as pentacene and P3HT.¹³ The lower values of the two parameters are mainly ascribed to the better quality of semiconductor/SiO₂ interface with low density of charge traps due to the hydrogen bond interaction between the $-\text{N}-\text{O}^{\cdot}$ of 1-imino nitroxide pyrene and the $-\text{OH}$ groups on the SiO₂ surfaces.¹⁴ The low threshold voltage and inverse subthreshold slope warrant the low-voltage operation of the OFETs.¹⁵ Slight contact resistance at low source–drain voltages can also be shown, most probably due to the 0.35 eV mismatch between the HOMO (5.45 eV) and the work function of Au (5.1 eV).¹⁶ The structure order and crystalline feature of the thin film were investigated by X-ray diffraction (XRD) and scan electron microscopy (SEM). From the XRD pattern, almost no reflection peak was observed, suggesting disordered orientation on the SiO₂/Si substrate. However, the OFETs showed high mobility. It is suggested that the molecules of the first layer are arranged regularly for the hydrogen bond interaction between $-\text{N}-\text{O}^{\cdot}$ of the molecules and $-\text{OH}$ on the SiO₂ surface, and the arrangement facilitates the transport of the carriers. The SEM image of the thin film revealed that vapor deposition afforded a uniform film, grains of near-regular shape and average size of $0.2 \mu\text{m}$. No large grain boundaries and relative special separation

were observed, which indicates that the film facilitates the carrier transport and is a good candidate for the semiconducting layer of the OFETs.

In summary, we succeeded in the fabrication of OFETs based on 1-imino nitroxide pyrene. The device can be operated within low voltage and shows *p*-type FET characteristics with excellent performance. To the best of our knowledge, this is the highest performance of OFETs based on the organic radicals.

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Supporting Information Available: Details of experimental procedures and additional data or spectra, information of OFET device fabrication, and X-ray crystal structure (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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