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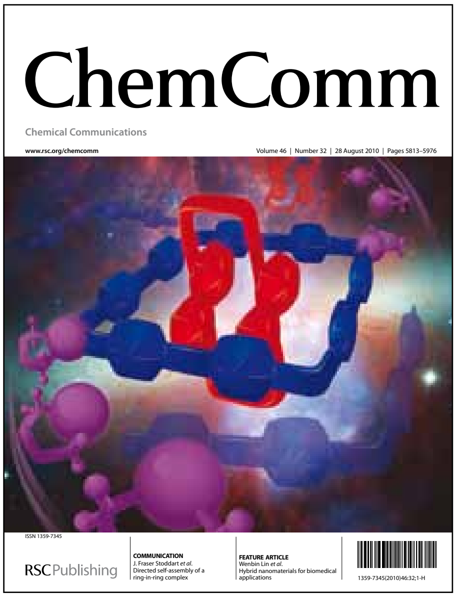

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ARTICLE TYPE

A Simple Nickel Bis(Dithiolene) Complex as an Excellent n-Type Molecular Semiconductor for Field-Effect Transistors

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Abstract: a simple nickel bis(dithiolene) complex has been developed as an excellent n-type molecular semiconductor for FETs, with electron mobility of 0.11 cm^{2}V^{-1}s^{-1} and on/off ratio of 2×10^6 despite its small π-conjugated system. Good FET stability in ambient condition has been also observed.

In the past decades, molecular semiconductors have received great attentions and undergone tremendous progress for fabrication of field effect transistors (FET) and complementary logic circuits. [1] Although some robust and efficient n-type materials have been realized, their development has still lagged behind that of p-type semiconductors by contrast.[2,3] The research on n-type molecular semiconductors are mainly focused on electro-negative substituted small molecules and polymers with π-conjugated structures, and relatively low air-stability and tedious synthetic procedures have restricted their development.[3]

Nickel bis(dithiolene) complexes has become one type of molecular semiconductors since the first nickel dithiolene charge transfer complex showing n-type behavior in 1994.[4] However, the FET performance of nickel dithiolenes were low, with mobilities ranging from 10^{-3} to 10^{-5} cm^2 V^{-1} s^{-1},[5] far behind organic conjugated molecules. To date, only a small number of nickel dithiolene semiconductors have been reported, and the research on their molecular design and structure-property relationship remain deficient.

Nickel dithiolene complexes usually possess square-planar configurations, and they can easily form an electron delocalized system with low LUMO energy level. Their properties and mode of the conjugations can be modulated by changing substitutions on the dithiolene part.[6] High electron mobility (2.8 cm^2 V^{-1}s^{-1}) determined by space-charge limited current (SCLC) technique was observed for one nickel dithiolene complex, but its field-effect mobilities were found to be over two orders of magnitude lower (1.3×10^{-3} cm^2 V^{-1} s^{-1}) than the SCLC values.[5e] Meanwhile, another square-planar nickel coordination compounds, bis(o-diiminobenzosemiquinonate) nickel complexes were reported to exhibit good p-type FET performance (with mobility of 3.8 × 10^{-2} cm^2 V^{-1} s^{-1}) or ambipolar transport behavior (with mobility of 4.3 × 10^{-3} cm^2 V^{-1} s^{-1} for holes and 1.6 × 10^{-2} cm^2 V^{-1} s^{-1} for electrons) with different metal electrodes and dielectric layers.[7] These facts suggest that much better FET performance of nickel dithiolene complexes might be achieved through molecular engineering and device optimizations.

In most cases, the nickel dithiolene complexes that have been studied for FET are bis(1,2-di-aryl-1,2-ethenedithiolato) nickel complexes (**Figure 1a**), there is no report on FET property of bis(1-aryl-1,2-ethenedithiolato) nickel analogues (**Figure 1b**). Based on the above information, we have recently designed and studied a bis(1-(4'-trifluoromethylphenyl)-1,2-ethenedithiolato) nickel complex **1** (**Figure 1c**) as a new n-type semiconductor. There are two considerations for this molecular design: 1) In 1,2-di-aryl substituted complex, the presence of the four outer aromatic groups is disadvantageous to the molecular packing due to the bulkiness of four substituents,[5d,8] while in a 1-aryl substituted complex, the steric effect is much less by removing two outer rings.[9] 2) Trifluoromethylphenyl ring has been one of the most widely used end-capped groups for n-type semiconducting materials, since trifluoromethyl group (-CF$_3$) can further lower the LUMO and is favorable for molecular packing and the film morphology.[10] It was found that the complex **1** exhibited high electron mobility over 0.1 cm^2 V^{-1} s^{-1} with on/off ratio up to 2 × 10^6. To the best of our knowledge, this is the best FET performance among square-planar nickel complexes.

As depicted in **Figure 1c**, complex **1** was conveniently synthesized with good yields and purified by recrystallization from chloroform. It was characterized by ^{1}H NMR spectroscopy,

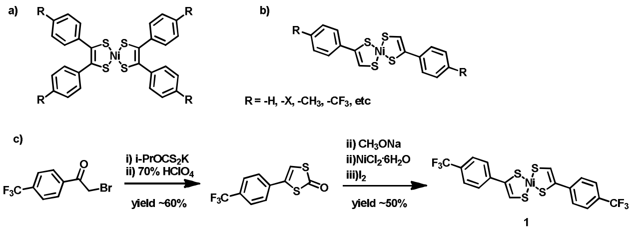

Figure 1. a) 1,2-di-aryl substituted nickel dithiolene complexes. b) 1-aryl substituted nickel dithiolene complexes. c) Synthesis of the complex **1**.

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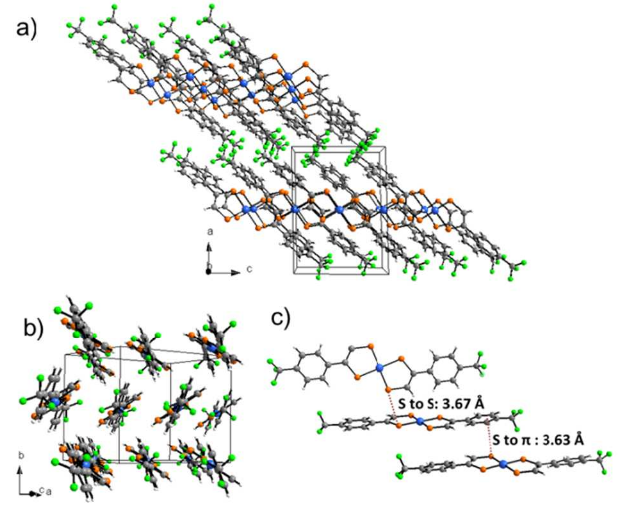

Figure 2. Crystal structure of the complex **1:** a) b-axis projection, b) herring bone packing motif, c) short contacts.

mass spectrometry, elemental analysis and single crystal structure (see Supporting Information for details, and its mono-anionic form $[Bu_4N]^+[\mathbf{1}]^-$ was also synthesized for comparison). The basic physical properties of **1** were characterized by thermo gravimetric analysis, UV-Vis-NIR absorption spectra and cyclic voltammograms (CV). Related figures and data are shown in Supporting Information (**Table S1**).

From the CV data, its HOMO and LUMO levels as well as band-gap can be estimated.[11] The complex **1** has very low LUMO levels (–4.51 eV) and narrow band-gaps (–1.08 eV), which are indicative of the electron-deficiency and electron delocalization. These results imply that the complex **1** may be an air-stable n-type semiconducting material.[5b] In addition, perfectly reversible and reproducible reduction process of **1** have been observed, which are favorable for electron transport.

Density Functional Theory (DFT) calculations were performed using the Gaussian 09 program at B3LYP level (with Lanl2dz pseudo potential basis set for Ni and 6-31+g(d) for all other atoms) to estimate the electron-density-distribution of frontier molecular orbitals as well as reorganization energy for the complex **1** (see Supporting Information for details). The HOMO is mainly located on the dithiolene ligands, and does not have any coefficient of nickel atom; while the LUMO incorporates both nickel atom and dithiolene part, demonstrating efficient LUMO delocalization. The reorganization energies of electron- and hole-transport of the complex **1** are calculated (**Table S2**). Its electron-transport reorganization energy is 0.20 eV, which is a quite small value compared to that of some electron-transport materials calculated at the same level.[12] According to Marcus theory, high electron mobility of the complex **1** may be achieved.[13]

Single crystals of the complex **1** as well as its mono-anionic form $[Bu_4N]^+[\mathbf{1}]^-$ were grown by slow evaporation from solutions in chloroform or THF, and their crystal structures were determined by X-ray crystallographic analysis.[14] In the crystal structure of the complex **1**, two dithiolene rings in the same molecule are strictly coplanar (the dihedral angle of two dithiolene rings in the complex **1** is 0°), while the dihedral angle between external 4'-trifluoromethylphenyl ring and the square-planar nickel dithiolene moiety is 34.5°. It should be noted complex **1** lies about an inversion centre, with the Ni atom on an inversion centre. As shown in **Figures 2a** and **2b**, the complex **1** has a herring bone packing motif with staggered layers. S–S contacts of 3.67Å and S–π contacts of 3.63 Å can be found in different directions (**Figure 2c**), thus substantial carrier transport path ways among neighboring molecules can be constructed.

Different from many nickel dithiolene complexes with paired crystal structures and triclinic crystal system,[5d,8,9a] the crystal of complex **1** exhibits monoclinic crystal system, and no dimerization was found in it. Since monoclinic crystal system usually exhibit better symmetry and more densely crystal packing than triclinic crystal system, and dimerized structures of these compounds may not be good for charge transport,[5d,14] better FET performance of complex **1** than some reported nickel dithiolene semiconductors has been expected.

In the crystal structure of $[Bu_4N]^+[\mathbf{1}]^-$ (Figure S4 in Supporting Information), the ions lie in general positions in the asymmetric unit and there is no crystallographically-imposed inversion symmetry as was found in the structure of complex **1**. Selected bond lengths and angles as well as dihedral angles in the complex **1** and $[Bu_4N]^+[\mathbf{1}]^-$ are listed in **Table S4** in Supporting Information. It can be seen that geometry changes between neutral (**1**) and mono-anionic ($[Bu_4N]^+[\mathbf{1}]^-$) forms are really small, implying small electron-transport reorganization energy, in agreement with the DFT results.

Semiconductive property of the complex **1** was investigated by FETs. Thin films were vacuum deposited on octadecyl-trichlorosilane-treated SiO_2/Si (OTS-SiO_2/Si) substrates and polystyrene-treated SiO_2/Si (PS-SiO_2/Si) substrates, respectively, at substrate temperatures (T_{sub}) of 20, 30, 70 or 100 °C. The Au source/drain contacts were deposited on the semiconducting layer through a shadow mask, affording a top-contact device configuration (see Supporting Information for more details). The devices were first tested in vacuum conditions. Inspiringly, high electron mobilities have been obtained, which are in the range of 0.01–0.18 $cm^2\ V^{-1}\ s^{-1}$ on both substrates. On OTS–SiO_2/Si substrates, the highest mobility is up to 0.18 $cm^2\ V^{-1}s^{-1}$, but the

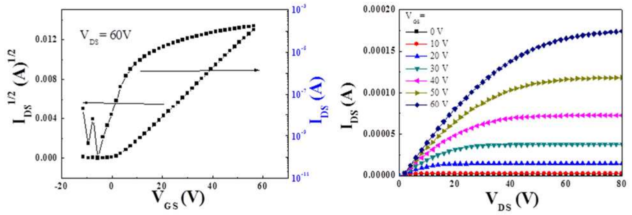

Figure 3. I–V characteristics of the complex **1** based FET prepared on PS-SiO_2/Si substrate deposited at T_{sub} = 70 °C, under nitrogen atmosphere: a) Plot of I_{DS} vs. V_{GS} for V_{DS} = 60 V. b) Plot of I_{DS} vs. V_{DS}.

Table 1. FET performances of the complex **1**

Substrates	T_{sub} /°C	$\mu/cm^2\ V^{-1}s^{-1}$	I_{on}/I_{off}
OTS-SiO_2	20	0.040	276
	30	0.18	363
	70	0.093	1200
	100	0.081	2600
PS-SiO_2	20	0.018	4400
	30	0.063	10^5
	70	0.11	2×10^6
	100	0.045	8×10^4

on/off current ratios are relatively low (<10^4). On PS–SiO_2/Si substrates, better switching characteristics of FETs can be achieved. When T_{sub}= 70 °C (**Figure 3**), thin film of the complex **1** exhibits excellent n-type FET performance with a mobility of 0.11 $cm^2\ V^{-1}\ s^{-1}$ and on/off ratio of 2 × 10^6. The device performances of the complex **1** are summarized in **Table 1**.

Except for the high charge carrier mobility, good stability in air is also a key parameter for the potential application of FETs. The on/off current cycle test was performed on one representative device (on PS-SiO_2/Si substrate) and a good stability was shown over 1000 test cycles (**Figure S7a**). Furthermore, FET performances of the complex **1** in ambient conditions have been examined. On PS-SiO_2/Si substrate at T_{sub} = 70 °C, the mobility (0.089 $cm^2\ V^{-1}\ s^{-1}$) and on/off current ratio (4 × 10^4) remain in a high level; and after the devices were stored in ambient conditions for about 30 days, the mobility showed little changing (μ/μ_0 > 0.82) and the current on/off ratio was still kept between 10^4 and 10^5 (**Figure S7b**). These results indicated good air stability of complex **1**, which implies its practical application value.

Atomic force microscopy (AFM) was taken to study the vacuum deposited films of the complex **1** (**Figures S8a** and **S8b**). Complex **1** forms interconnected films. The grain size increases and the grain boundaries become more obscure when increasing substrate temperatures. However, the device performance is not further enhanced at the highest T_{sub}, probably because the carrier trap size also becomes larger.[15]

To gain insight into the film structures, XRD were carried out for thin films of the complex **1** (**Figures S8c** and **S8d**).On PS-SiO_2/Si substrates, a series of sharp peaks are observed, and strongest diffractions appears at T_{sub} = 70 °C, consistent with the T_{sub} at which the best FET performance appeared; on OTS-SiO_2/Si substrates the intensities of diffractions are relatively weak. The first diffraction peak (5.28 °) is corresponding to layer spacing of 16.8 Å, close to the length of the molecule observed in the X-ray single crystal structure of the complex **1** (17.4 Å). The results reveal good crystallinity and ordering of the thin film of the complex **1**, and may imply that the molecules take edge-on molecular orientation in the film.

It is worth noticing that the complex **1** has a simple structure with less extended π-conjugation compared to most of organic semiconductors, such n-type FET performance is unprecedented. In addition, the ease of synthesis and high ambient stability of these materials will be ideal for low-cost production and practical application. Therefore, these may open up a new window for the development of high-performance n-type semiconductors.

In summary, a simple nickel bis(dithiolene) complex **1,** bis(1-(4'-trifluoromethylphenyl)-1,2-ethenedithiolato) nickel, has been designed and synthesized. Despite its small π-conjugated system, thin film of **1** has shown excellent n-type field-effect transistor response, with electron mobility of 0.11 $cm^2\ V^{-1}\ s^{-1}$ and on/off ratio of 2 × 10^6. Good FET stability in ambient condition has been also observed. These results suggest the new design strategy and bright future of square-planar nickel complexes for molecular electronics. Further work is in progress to investigate the structure-property relationships.

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The table of contents entry

A exploratory research on a nickel bis(dithiolene) complex — bis(1-(4'-trifluoromethyl- phenyl)-1,2-ethane -dithiolato) nickel as n-type molecular semiconductor is presented. Despite its simple structure and small π-conjugated system, thin film of it has shown excellent n-type field-effect transistor response, with electron mobility of 0.11 $cm^2V^{-1}s^{-1}$ and on/off ratio of 2×10^6. Good FET stability in air has been also observed.

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