# Introduction of $F_4$-TCNQ/$MoO_3$ layers for thermoelectric devices based on pentacene*

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We introduced a dual electron accepting layer composed of tetrafluoro-tetracyanoquinodimethane ($F_4$-TCNQ) and $MoO_3$ for thermoelectric devices based on a pentacene layer. We found that the power factor is enhanced by placing an $F_4$-TCNQ layer directly in contact with the pentacene layer and it is also enhanced by placing a $MoO_3$ layer between the $F_4$-TCNQ layer and the Au electrode. By examining the contact resistance using a field effect transistor and a hole-only diode, we confirmed that the hole injection is improved due to the reduction of contact resistance at the interface between the $MoO_3$ layer and the Au electrode.

**Keywords:** thermoelectrics, pentacene, $MoO_3$, contact resistance

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## 1. Introduction

Thermoelectrics can harvest electricity directly from the heat generated from natural resources or waste heat and provide reliable, environment-friendly energy conversion. It gives a promising solution to current energy and environmental problems, and many kinds of inorganic semiconductors have been developed, some of which have been commercialized.[1–5] Recently, organic thermoelectric materials have attracted considerable attention due to the various possibilities of molecular structures for high performance thermoelectric devices,[6–8] and the capabilities of non-toxic and flexible large area fabrication. As a consequence, the potential applications are being extended to infrared light detectors, gas sensors, and precise temperature control systems.[9–13] Their relatively low electrical conductivity and low power factors have limited their practical application as an energy generator. The efficiency of thermoelectrics depends on a combination of material properties quantified by the thermoelectric figure of merit $ZT = S^2\sigma T/k$, or the power factor $\mathrm{PF} = S^2\sigma$, where $S$ is the Seebeck coefficient, $\sigma$ is the electronic conductivity, $T$ is the absolute temperature, and $k$ is the thermal conductivity. While $S$ and $\sigma$ are primarily determined by the material's electronic structure, $k$ is composed of both electron and phonon contributions. The thermoelectric figure of merit of inorganic thermoelectrics has been increased in the past decade to values higher than 2, while the best result for organic thermoelectrics is limited to 0.25.[14–16]

In parallel to the material development, it is also important to develop device architectures leading to high $ZT$. Besides, there are lots of parasitic losses in the devices that lower the efficiency. In particular, making a good contact at the interface region in devices is a crucial issue for most organic-based devices, and the thermoelectric devices are no exception. In this paper, we study the phonon and electron transport in the interfacial regions of thermoelectric devices based on a pentacene layer. We study two different acceptors to advance our understanding for designing high-performance thermoelectric devices. We choose pentacene as the p-type thermoelectric material for its excellent charge transport property and low thermal conductivity of about 0.48 W/mK at room temperature.[12] Tetrafluoro-tetracyanoquinodimethane ($F_4$-TCNQ) and $MoO_3$ are chosen as the acceptors for their strong electron accepting properties.[17–20] High Seebeck coefficients in the range of 400–700 μV/K are obtained in pentacene-based thermoelectric devices. When a $MoO_3$ layer is placed between the $F_4$-TCNQ layer and the Au electrode, the power factor is apparently improved, indicating the reduction of the contact resistance between the $MoO_3$ layer and the Au electrode.

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## 2. Experimental details

Figure 1(a) shows the basic thermoelectric device structure used as a reference in our study. The thickness of pentacene was 8 nm. We kept the total thickness of the acceptor layer be 3 nm. Pentacene and acceptor layers were thermally deposited on self-assembled monolayers (SAM) of hexamethyldisilazane modified glass substrates in a vacuum chamber, followed by the thermal deposition of Au for use as a contact. The deposition rates of pentacene, the acceptors, and the gold electrode were 0.02 nm/s, 0.01 nm/s, and 0.2 nm/s, respectively. The main measurement of all thermoelectric devices was carried out by using the method reported in our previous paper.[12] We used an infrared thermography system (Advanced Thermo TVS-500EX, NEC Avio Infrared Technologies Co., Ltd.) to more accurately detect the temperature difference between the hot and the cold areas.

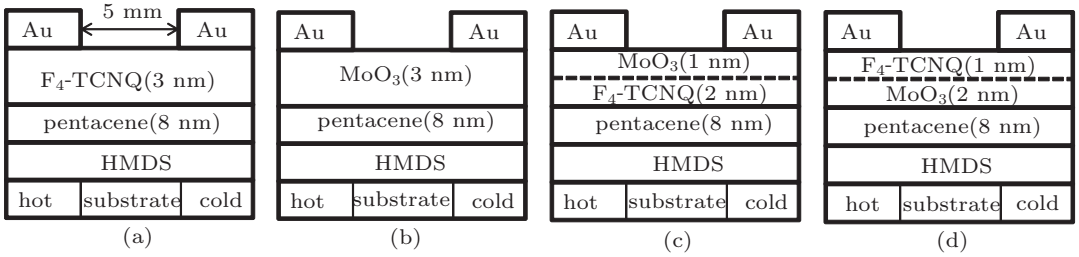



**Fig. 1.** An illustration of different pentacene-based thermoelectric device structures in our study: (a) device 1, (b) device 2, (c) device 3, (d) device 4.

## 3. Results and discussion

Four devices were prepared depending on the different acceptor layers, 3 nm $F_4$-TCNQ, 3 nm $MoO_3$, 2 nm $F_4$-TCNQ/1 nm $MoO_3$, and 2 nm $MoO_3$/1 nm $F_4$-TCNQ, named as device 1, device 2, device 3, and device 4, respectively. The device structures of the four thermoelectric devices are shown in Fig. 1. The thermoelectric parameters of the four devices are summarized in Fig. 2. From the electrical conductivity in Fig. 2(a), we find that the electrical conductivity of device 2 is significantly decreased compared to that of device 1, from 0.64 S/cm to 0.03 S/cm when using $MoO_3$ as the acceptor layer instead of the $F_4$-TCNQ layer, which results in a lower power factor of 1.13 μW/mK$^2$. For device 3 and device 4, we alternate the interface of pentacene and the acceptor layers, that is, the pentacene layer contacts with the $F_4$-TCNQ layer in device 3 and the pentacene layer contacts with the $MoO_3$ layer in device 4. Comparing their performance, we find a decrease of electrical conductivity in device 4, indicating that it is not good to have the pentacene layer contacting with the $MoO_3$ layer directly, even though there is a strong interaction between pentacene and $MoO_3$.[21,22] In addition, we find that the conductivity is slightly enhanced when a $MoO_3$ layer is placed between the $F_4$-TCNQ layer and the Au electrode, as shown in device 3. The maximum conductivity of 0.77 S/cm and a Seebeck coefficient of about 540 μV/K are demonstrated. Thus, the power factor is improved from 15.2 μW/mK$^2$ to 22.5 μW/mK$^2$ using a 1 nm $MoO_3$ layer contacting the Au electrode. It is interesting that the Seebeck coefficient is not sacrificed with the increase of the electrical conductivity. In typical doped organic semiconductors, the general pattern is known as a reverse relationship, that is, with the increase of the electrical conductivity, the Seebeck coefficient is decreased, and vice versa.[12,23] The Seebeck coefficient is related to the electrical conductivity in a very complicated way which involves the change of the Fermi energy level and the introduction of excess hole traps. This shows that the relevant relationship between Seebeck coefficient and electrical conductivity in thermoelectric devices with a bilayer structure might be different from that with a doping structure.

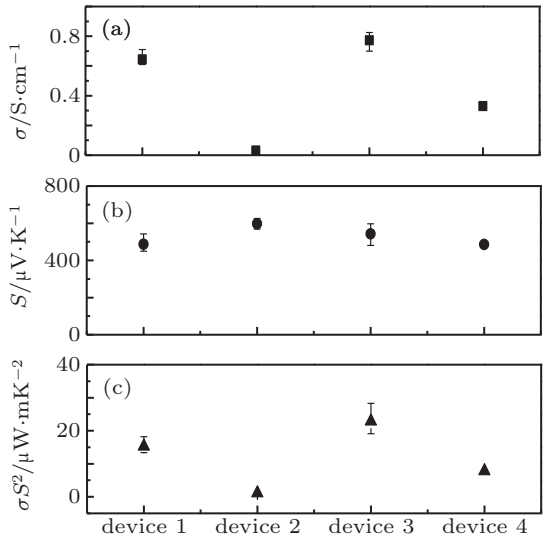



**Fig. 2.** Thermoelectric performance of four devices with different acceptor layers measured at room temperature: (a) electrical conductivity, (b) Seebeck coefficient, and (c) power factor.

In order to understand the performance improvement in device 3 with a $MoO_3$ layer as a modifying layer, we consider the electronic properties of the $MoO_3$ layer. $MoO_3$ has an elec-

tron affinity of 6.7 eV[22] and $F_4$-TCNQ has an electron affinity of 5.24 eV,[21] greater than the highest occupied molecular orbital (HOMO) level of pentacene (5.0 eV).[24] Therefore, there is efficient electron transfer from pentacene to the acceptors. Au is one of the most promising metal electrodes for pentacene-based thermoelectrics due to the small mismatch between the work function of Au and the HOMO level of pentacene, which is also demonstrated in organic field-effect transistors (OFETs).[25,26] However, the interface dipole is easily formed immediately when Au is deposited onto the pentacene layer. Thus, by placing an $F_4$-TCNQ layer, the hole-injection barrier can be alleviated, and the $MoO_3$ layer may further decrease the hole-injection barrier.

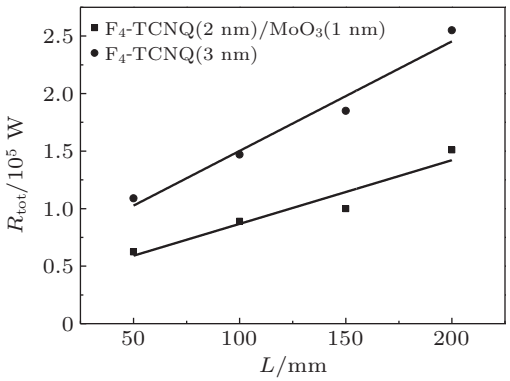



**Fig. 3.** Total resistance $R_{tot}$ versus channel length $L$ for the FETs with and without the $MoO_3$ outside layer, measured at $V_g = 0$ V for various channel lengths. The $R_c$ is evaluated by extrapolating the relation $R_{tot}$ versus $L$ to $L = 0$.

FET test structures were constructed to estimate the contact resistances of device 1 and device 3 in order to understand the improvement of the electrical conductivity. We prepared the samples on heavily doped Si substrates covered with a $SiO_2$ dielectric layer, employing the same treatment and deposition conditions as for the Seebeck coefficient and conductivity samples. Devices with various channel lengths were fabricated. The channel lengths are 50 μm, 100 μm, 150 μm, and 200 μm, respectively. Total resistance $R_{tot}$ versus channel length $L$ for the FETs with and without the $MoO_3$ outside layer measured at $V_g = 0$ V for various channel lengths is shown in Fig. 3. The measured resistance $R_{tot}$ of the FET can be simplistically viewed as a series combination of the channel resistance $R_{ch}$ and the parasitic source and drain contact resistances $R_c$ ($R_c = R_S + R_D$). From the resistance studied in Fig. 3, it is clear that the total resistance is decreased when we put a 1 nm $MoO_3$ layer between the $F_4$-TCNQ layer and the Au electrode. We find that the contact resistance is reduced from $5.5\times10^4$ Ω to $3.14\times10^4$ Ω by using the $MoO_3$ modifying layer. We also fabricated hole-only diodes with and without a $MoO_3$ layer to clarify the importance of the $MoO_3$ layer. The device structures are ITO/α-NPD (25 nm)/pentacene (50 nm)/$F_4$-TCNQ (3 nm)/Au (100 nm) and ITO/α-NPD (25 nm)/pentacene (50 nm)/$F_4$-TCNQ (2 nm)/$MoO_3$ (1 nm)/Au (100 nm). The current density versus voltage characteristics of hole-only devices are shown in Fig. 4. It is clear that the current density is larger in the device with the $F_4$-TCNQ/$MoO_3$ layer, demonstrating the improvement of the hole injection.

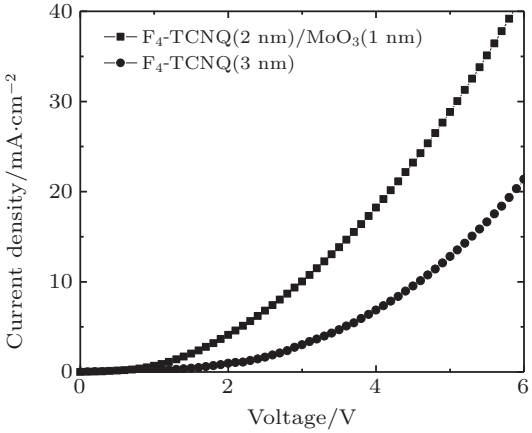



**Fig. 4.** Current density versus voltage characteristics of hole-only diodes with and without the $MoO_3$ layer. The device structures are ITO/α-NPD (25 nm)/pentacene (50 nm)/$F_4$-TCNQ (3 nm)/Au (100 nm) and ITO/α-NPD (25 nm)/pentacene (50 nm)/$F_4$-TCNQ (2 nm)/$MoO_3$ (1 nm)/Au (100 nm).

## 4. Conclusion

In conclusion, $F_4$-TCNQ and $MoO_3$ were studied as the electron accepting layer for thermoelectric devices based on a pentacene layer. We demonstrated that the thermoelectric performance can be improved by decreasing the contact resistance. The power factor was enhanced using a $MoO_3$ modifying layer between the $F_4$-TCNQ layer and the Au electrode.

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