

A Cyclic Triphenylamine Dimer for Organic Field-Effect Transistors with High Performance

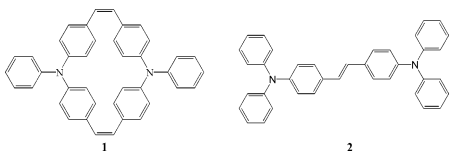
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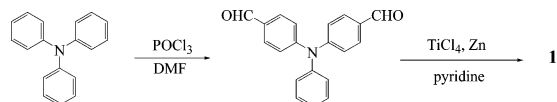
Since the first report on organic field-effect transistors (OFETs) in 1986,¹ OFETs have attracted increasing interest during the past decades because of their easier fabricating and lower cost compared with traditional silicon-based transistors.² They can be ideally used in large-area, compact, and lightweight plastic circuits on flexible substrates in electronic devices.³ In recent years, great progress has been made on both the fabrication methods of OFETs and the synthesis of high-performance semiconductor materials.⁴ Especially, some typical organic materials have achieved mobilities beyond $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,^{4a} that can even be compared with mobilities of amorphous-silicon devices. Despite this remarkable development, the design of new semiconductors with high OFET performances and a better understanding of the relationship between the structure and the property are still the major challenges in modern molecular electronics.

Triarylamine-based organic semiconductors have been widely studied as hole transport materials for optoelectronic applications (e.g., xerography, organic light-emitting diodes, etc.).⁵ These materials possess attributes, such as good electron-donating ability and reasonably high ambient stability, that meet well with the requirements for OFETs application. However, most of the very recent reports presented low FET mobilities owing to their amorphous nature in solid state.⁶ Here, we would like to report a new FET semiconductor based on triarylamine units with a macrocyclic structure, compound **1**. Different from those linear, star-shaped or dendrimeric triarylamines for amorphous materials, a closed ring and steric crowded structure will restrict the rotation of the phenyl groups and improve the molecular ordering in the solid state, that will facilitate the charge carrier transportation. Ethylene was chosen as linkage for its ability to effectively extend the π -conjugated length, reduce the band gap, and tune the electrical properties.^{4g,7} For comparison, a linear analogue (**2**) was investigated simultaneously.



The synthesis of compound **1** is summarized in Scheme 1. It can be conveniently synthesized by McMurry coupling reaction from 4,4'-diformyltriphenylamine.⁸ Although the yield of **1** (9.0%) was a little lower, it was only a two-step reaction that can be operated in a large scale. Compound **2** was synthesized according to the literature.⁹ Both **1** and **2** have large solubility in common organic solvents, such as CH_2Cl_2 , chloroform, and toluene. They

Scheme 1. Synthesis of **1**



can be easily purified by recrystallization and gradient sublimation. Thermogravimetric analysis (TGA) measurements gave the thermal decomposition temperatures (T_d), 338 °C for **1** and 400 °C for **2**, indicating their good thermal stability to be used as active layers in OFETs.

Single crystals of **1** were obtained by the slow evaporation of solvent from dichloromethane solution. The molecular structure of **1** was shown in Figure 1a; it could be seen that four *p*-phenylene units were linked by two nitrogen atoms and ethylene bridges to form a macrocycle. These linking atoms adopted coplanar structure with each phenylene ring canting out of this plane with torsion angles from 34.60 to 50.35°. The molecules in the crystal packed into columns along the *b*-axis direction as shown in Figure 1b. These columns then stacked in a so-called “layer-by-layer” pattern both in *a*- and *c*-axis directions. Such column and layer-by-layer packing manner should favor efficient hole transportation.

The vapor-deposited thin films of **1** and **2** on SiO_2/Si substrates were characterized by X-ray diffraction (XRD) (Figure S10). The XRD pattern of thin films of **1** deposited at 22 °C displayed a series of sharply resolved peaks assignable to multiple (00*l*) reflections, indicating that **1** formed highly crystalline layer-structure in thin films. It shows an interlayer peak at $2\theta = 6.86^\circ$, corresponding to a *d*-spacing of 12.87 Å. This value is almost identical to that of the layer spacing along the *c*-axis direction in the single crystal (13.05 Å), showing that the molecular packing in the thin films was almost the same as that in single crystals. On the other hand, XRD results of **2** exhibited no reflection peaks, indicating that the films were almost amorphous and the molecules were randomly oriented. Therefore, a significant improvement of molecular ordering in the evaporated thin films was achieved by molecule **1** with ring architecture.

AFM images show complementary information about these films (Figure S11). As we know, the morphological features of thin films depend significantly on substrate temperature (T_{sub}). At 22 °C **1** formed large-area and interconnected crystalline domains with an average diameter of 1 μm , which were very helpful to hole transportation. The crystal grains grew in size and elongated in shape with increasing substrate temperature. However, film discontinuities and large gaps increased as well, which had large negative effect on OFETs. Contrastly, **2** formed films with many discontinuities at each temperature, exhibiting poor hole transport properties.

OFET devices were fabricated using a top-contact geometry on a layer of SiO_2 dielectrics (450 nm). Gold electrodes with W/L of

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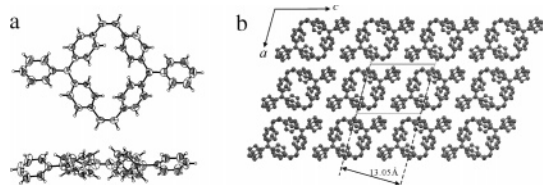


Figure 1. (a) Top view and side view of the molecular structure of compound **1**. (b) Stacking pattern of **1** in the crystal viewed along the *b*-axis (hydrogen atoms were omitted for clarity).

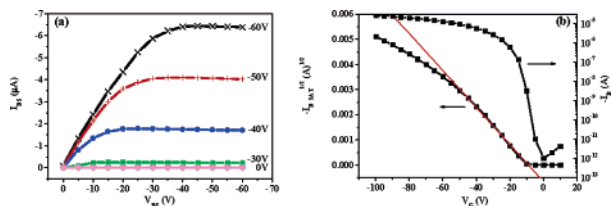


Figure 2. (a) Plots of drain-to-source current (I_{DS}) vs drain-to-source voltage (V_{DS}) for the FET of **1** fabricated on SiO_2 at 22 °C. (b) $-I_{DS}$ and $(-I_{DS})^{1/2}$ vs V_G plots for the same device at V_{DS} of -60V .

Table 1. The Performance of FETs Based on **1** and **2** Prepared at Different Temperatures of the Substrate (T_{sub})

compound	T_{sub} (°C)	mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	on/off ratio
1	12	6×10^{-3}	10^6
1	22	1.5×10^{-2}	10^7
1	60	1×10^4	10^5
2	22	2×10^4	10^5

3.0 mm/0.05 mm were applied after organic film deposition by using shadow mask. The output characteristics of these devices are shown in Figure 2 and Table 1. These materials all performed as p-type semiconductors at room temperature.

As expressed in Table 1, the hole mobility of **1** deposited at 22 °C was found to be $1.5 \times 10^{-2} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, which was 100 times as high as that of **2** under the same condition. To the best of our knowledge, this performance is one of the best results of OFETs based on triarylamine derivatives. Similar to what had been observed in many OFETs, the FET performance of **1** varied with T_{sub} . It was related to the change in morphological features as noted by AFM analysis. When T_{sub} became higher, the discontinuities increased, resulting in a poor FET performance. The on/off ratios of **1** and **2** were high, because both of them had very low off currents in the pA range.

To understand the relationship between the structure and the property, we employed the Marcus electron transfer theory and an incoherent Brownian motion model to calculate the hole mobilities¹⁰ (see Supporting Information) based on the single-crystal structures of compound **1** and **2**. The intermolecular electronic couplings were obtained by directly evaluating the dimer Fock matrix with the unperturbed monomer's molecular orbitals,¹¹ and the reorganization energies were performed at the density-functional theory (DFT) level with the B3LYP function and a 6-31 g(d) basis set. The room-temperature hole-diffusion mobility was obtained to be $2.1 \times 10^{-2} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for **1** and $1.9 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for **2**. These values compared very well with the experimental results. It suggested that the macrocyclic structure of compound **1** was more favorable to hole transportation.

In summary, the molecular ordering of ethylene linked triphenylamine dimers in vapor deposited thin films changed significantly when the molecular structure changed from linear to cyclic

type. The cyclic structure also led to a significant reduction of the reorganized energy. Because of the two facts, compound **1** displayed an improved mobility in FETs as compared to that of linear compound **2**. Another attractive character of FETs based on **1** is a high on/off ratio up to 10^7 . Considering the intrinsic stability of triphenylamine-based materials, this result may provide a new promising choice for organic semiconductors for OFETs. We are currently investigating modifications of these molecules to improve the FET performance.

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Supporting Information Available: Details of experimental and computational procedures, X-ray crystal structure (CIF) of compound **1**, additional data or spectra, information of OFET device fabrication, XRD, and AFM. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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