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Organic field-effect transistors fabricated with $N,N'$-substituted dialkyl-1,3,8,10-tetramethylquinacridone compounds

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A series of robust and inexpensive $p$-type organic semiconductors, 1,3,8,10-tetramethyl quinacridone compounds was prepared. These quinacridone compounds bearing $N,N'$-disubstituted long $N$-alkyl chains self-organize into highly oriented crystalline films, leading to high performance organic thin film transistors with the best field-effect mobility, on/off ratio, and threshold voltage being $1.6 \times 10^{-1}$ cm$^2$ V$^{-1}$ s$^{-1}$, $1 \times 10^4$, and $-17$ V, respectively. The effects of methyl substituent and $N$-alkyl chain length of the quinacridone compounds together with the molecular packing on the field-effect mobility are discussed. © 2009 American Institute of Physics. [doi:10.1063/1.3233961]

Organic thin film transistors (OTFTs) have important applications in electronics including sensors, light-emitting devices, and memory devices. Compared with silicon-based devices, the fabrication process of OTFT is simple and low cost and has a high compatibility with conventional soft lithography. To develop inexpensive and robust organic semiconductor materials that possess high field-effect mobility, much attention has been focused on $p$-type pentacene and derivatives. Nonetheless, multisteps are needed for the synthesis and modification of pentacene compounds. In the context of developing OTFT materials, $\pi$-conjugated organic compounds with a rigid and fused-ring structure are of particular interest.

Quinacridone compounds are chemically stable and widely utilized as light-emitting and photoconductive materials. These materials are relatively inexpensive, soluble in common organic solvents, and could be readily modified. In this work, a series of $N,N'$-dialkyl quinacridone (QA) compounds—QA-C$_2$, QA-C$_4$, QA-C$_6$, and QA-C$_8$—and $N,N'$-dialkyl-1,3,8,10-tetramethylquinacridone (TMQA) compounds—TMQA-C$_4$, TMQA-C$_6$, TMQA-C$_8$, and TMQA-C$_{16}$ (Fig. 1)—were prepared according to the literature methods. The charge transport properties of these compounds for OTFT applications have been investigated.

The QA and TMQA compounds were used to fabricate organic transistors using a bottom-contact substrate-gate structure by high-vacuum evaporation and measured using the same literature method. The surface morphology and crystallinity of the thin films in the OTFT devices fabricated with these compounds were studied by scanning electron microscopy (SEM) and grazing incidence x-ray diffraction (GIXRD).

The thermal stability of the QA or TMQA compounds and performance of the as-fabricated devices are listed in the Table I. Most of the compounds examined have a decomposition temperature ($T_d$) in the range of 373–416 °C. Interestingly all TMQA compounds exhibited $p$-type field-effect behavior but all QA compounds exhibited no field-effect behavior. TMQA-C$_4$ showed a hole mobility ($\mu$) of $2.4 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, and $3.0 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ for TMQA-C$_6$ and TMQA-C$_8$. However, further increase in the $N$-alkyl chain length led to a decrease in the mobility value, as revealed in the case of TMQA-C$_{16}$ ($\mu = 2.1 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$). As depicted in Table I, the thin films derived from QA-C$_2$, QA-C$_4$, QA-C$_6$, and QA-C$_8$ showed no field effect. Octadecyltrichlorosilane (OTS) was deposited onto the substrate prior to the OTFT device fabrication to reduce the hydrophilicity of the SiO$_2$ surface. Figure 2 shows the output and transfer characteristics of TMQA-C$_8$-based device with OTS-treated SiO$_2$/Si substrate before and after 100 cycles measurement. Upon increasing the gate voltage $V_g$, the drain current $I_d$ increases, revealing a $p$-type field-effect transistor (FET) behavior. The fresh sample showed a mobility of 0.16 cm$^2$ V$^{-1}$ s$^{-1}$ and current on/off ratio of $10^4$. After 100 cycles measurement, the shape of the successive transfer curve remained unchanged, revealing an unchanged threshold voltage $V_t$, and the output curve remaining.$^{9}$

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Fig. 1. Chemical structures of QA and TMQA compounds.

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showed a decrease in the saturated current by less than 10% and a mobility of 0.15 cm² V⁻¹ s⁻¹ corresponding to less than 10% decrease when compared with the initial mobility value. In addition, the devices could be operated under open atmosphere at room temperature and there was no change in the device performance. We did transient measurements on a TMQA-C₈-based FET device where a constant voltage was applied to the gate and drain (−40 V), while the current was measured as a function of time on the TMQA-C₈-based FET for more than 100 cycles. No decrease in the channel current was observed. This device was kept in a glovebox. After a period of 2 years, this device showed a mobility of 0.14 cm² V⁻¹ s⁻¹ corresponding to less than 0% decrease when compared with the initial mobility value, revealing the device stability.

Both crystallinity and morphology play important roles in the FET performance. FET behavior is usually observed for those materials that exhibit a regular crystalline packing arrangement. To acquire structural information, GIXRD patterns of vacuum-deposited thin films of QA and TMQA compounds deposited on SiO₂/Si substrate were recorded. In general, the QA-C₂ and QA-C₄ compounds formed thin films that displayed broad peaks corresponding to ~10% decrease in the initial mobility value, revealing the device stability.

FIG. 2. (Color online) The current-voltage characteristics. (a) Output and (b) transfer characteristics of bottom-contact OTFT fabricated with TMQA-C₈ before and after 100 cycles measurement (with OTS treatment, channel length of 40 μm, and width of 3000 μm).

FIG. 3. (Color online) GIXRD patterns of vacuum-deposited thin films of (a) QA compounds and (b) TMQA compounds (the peak positions are shown in a 2θ scale).

Maximum of ~0.8°–1.0° 2θ and weak diffraction peaks (<100 counts/s), revealing the poor crystallinity and almost amorphous film structure [Fig. 3(a)]. The GIXRD pattern of the QA-C₈ thin film revealed two molecular orientations (2θ≈6.36° and 2θ≈7.75°) [Fig. 3(a)], both of which caused insulating effect with no FET behavior eventually observed. Although the film of QA-C₆ exhibited a single sharp diffraction peak, the lack of FET behavior could be attributed to film morphology in which case crystalline grains were found to be loosely packed as discussed in the latter section. In contrast, all TMQA thin films exhibited a strong single diffraction peak, revealing that the films were highly crystalline and textured with well-ordered molecular alignment in one favorable direction. The GIXRD pattern of the TMQA-C₈ thin film displayed a diffraction peak at 7.01° (2θ) corresponding to an interplanar d-space of 12.6 Å, which is close to the molecular size (approximately 13.0 Å derived from the single crystal x-ray data). The d-space values of TMQA-C₆ (13.7 Å), TMQA-C₈ (17.0 Å), and TMQA-C₁₆ (22.0 Å) thin films reflect that the d-space value increases with increasing N-alkyl chain length. All these d-space values are consistently shorter than the molecular size of the corresponding compounds (17.9 Å for TMQA-C₆, 22.9 Å for TMQA-C₈, and 42.9 Å for TMQA-C₁₆), which were estimated from the assumption that the N-alkyl chains have effective length of 1.2 Å per CH₂ unit and adopted all-trans configuration, similar to that found in the x-ray crystal structure of TMQA-C₈. All TMQA compounds, except TMQA-C₄, have their molecular sizes larger than the observed d-space values, attributed to mutual interdigitation of the N-butyl chains throughout the neighboring molecular stacks.

The surface morphology of these thin films was revealed by their SEM images. As depicted in Fig. 4, the QA-C₄ [Fig. 4(b)] and QA-C₆ [Fig. 4(c)] thin films revealed discontinuous flat grains with considerable grain defects; consequently, the loosely packed crystalline grains led to no device performance. The as-deposited QA-C₂ film was almost covered by

TABLE I. Thermal stability and field-effect characteristics of TMQA compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>T_d (°C)</th>
<th>μ (cm² V⁻¹ s⁻¹)</th>
<th>I_on/I_off</th>
<th>Threshold voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMQA-C₄</td>
<td>375</td>
<td>2.4x10⁻³</td>
<td>1x10⁴</td>
<td>−4</td>
</tr>
<tr>
<td>TMQA-C₆</td>
<td>376</td>
<td>5.0x10⁻³</td>
<td>1x10²</td>
<td>−12</td>
</tr>
<tr>
<td>TMQA-C₈</td>
<td>388</td>
<td>3.0x10⁻²</td>
<td>1x10⁴</td>
<td>20</td>
</tr>
<tr>
<td>TMQA-C₁₆ (OTS-treated)</td>
<td>...</td>
<td>1.6x10⁻¹</td>
<td>1x10⁴</td>
<td>−17</td>
</tr>
<tr>
<td>TMQA-C₁₆</td>
<td>416</td>
<td>2.1x10⁻³</td>
<td>1x10²</td>
<td>−27.5</td>
</tr>
<tr>
<td>QA-C₂</td>
<td>375</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>QA-C₄</td>
<td>406</td>
<td>...</td>
<td>...</td>
<td>...</td>
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<tr>
<td>QA-C₆</td>
<td>393</td>
<td>...</td>
<td>...</td>
<td>...</td>
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<tr>
<td>QA-C₈</td>
<td>373</td>
<td>...</td>
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the aryl hydrogen atoms of QA-C4 merely lead to weak in-
hibit arrangement of molecules in the solid phase whereas
showed that replace an ethyl group by a methyl group
with platinum
21
by continuous crystalline grains
SiO2
termolecular interactions
FIG. 5. SEM images of film samples made from
platelike grains [Fig. 4(a)] and the QA-C8 film was covered by
continuous crystalline grains [Fig. 4(d)], whereas the thin
films of TMQA compounds revealed continuous tightly
packed crystals (Fig. 5) and this is favorable for charge trans-
port. Upon increasing the N,N’-dialkyl chain length from
N-butyl in TMQA-C4 to N-octyl in TMQA-C8, TMQA-C8
thin film was found to have a densely packed crystal grain
texture with little defect content.

The thin films of all QA compounds were poorly crys-
talline [Fig. 3(a)], consistent with the lack of field-effect mo-
bility, whereas thin films of all TMQA compounds have a
good field-effect mobility. This should be attributed to the
effect of the peripheral 1,3,8,10-tetramethyl groups at
the quinacridone core. The four C–H
b
π–π stacking interactions consequently leading to a high
mobility of 0.32 cm2 V−1 s−1.15 Among all QA and TMQA
compounds, the TMQA-C6 thin film showed the strongest
diffraction peak at 5.17° (2θ) (Fig. 3), revealing that this film
had the highest degree of crystallinity. The unique spatial
orientation of TMQA-C6 molecules might reinforce the lat-
eral molecular stacking parallel to the surface of the sub-
strate, facilitating the in-plane charge transport of the film.18
Therefore, the TMQA-C6 thin film with a good morphology
(Fig. 5) has the best field-effect mobility. But further increase
in the N-alkyl chain as in the case of TMQA-C10, leads to a
decrease in the field-effect mobility. The long N-alkyl chain
of TMQA-C16 decreases the molecular packing, leading to a
low crystallinity [Fig. 3(b)] and a low field-effect mobility.

In summary, a series of QA and TMQA was synthesized to
fabricate OTFTs by vacuum deposition method. The
charge transport properties are strongly affected by the sur-
f ace morphology, crystallinity, and molecular packing of the
thin film. The crystal packing and field-effect mobility of
thin films of TMQA compounds are affected by the length of
N-alkyl chains. TMQA-C8 was found to be a simple and
low-cost organic semiconductor for the fabrication of OTFT
device with potential practical application.

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