Organic Phototransistors Based on Self-Assembled Microwires of n-Type Distyrylbenzene Derivative

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Abstract: Molecular design and crystallinity control are important issues for the development of high-performance organic optoelectronic devices. Here, a highly photo-responsive n-type organic small molecular semiconductor, (2Z,2Z)-3,3′-(2,5-dimethoxy-1,4-phenylene)bis(2-(3,5-bis(trifluoromethyl)phenyl)acrylonitrile) (DM-R), was synthesized and the photoelectronic properties of self-assembled DM-R microwire organic phototransistors (MW-OPTs) were studied. Significant enhancement in the electron mobility ($\mu_e$) of MW-OPTs ($\mu_e$: 0.16 cm$^2$V$^{-1}$s$^{-1}$) was observed as compared to thin-film-OPTs ($\mu_e$: 2.7 × 10$^{-3}$ cm$^2$V$^{-1}$s$^{-1}$), most likely due to the single-crystalline nature of the self-assembled MWs. Moreover, the photoresponsivity of MW-OPTs showed 23.53 (A W$^{-1}$), which was 130 times higher than that of thin-film-OPTs (0.18 A W$^{-1}$). Furthermore, the MW-OPTs exhibited stable photoswitching properties and a faster charge accumulation/release rate than those of thin-film-OPTs. The results obtained herein demonstrate a facile solution-based approach for the fabrication of high-performance n-type organic MW-OPTs and provide a systematic analysis platform of the photo-generated charge carrier dynamics.

Introduction

Organic optoelectronic devices such as organic phototransistors (OPTs),[1–4] photovoltaic cells,[5–8] organic light-emitting diodes,[9–12] photodiodes,[13–16] lasers,[17–19] and memory devices[20–21] have attracted great interest owing to their high potential for use in flexible, low-cost, large-scale, and lightweight electronic applications. Although significant progress has been made to enhance their performance through the continued development of new materials and device configurations, further improvement of device efficiency is still necessary for commercialization.

Recently, one-dimensional (1-D) organic nano/microwires (NWs/MWs) self-assembled from conjugated small molecules or polymers have often been used for a wide range of optoelectronic applications, as they are highly suitable active materials for device miniaturization, low-cost fabrication, and high mechanical flexibility.[22–27] In contrast to amorphous or polycrystalline thin films, 1-D crystalline organic NWs/MWs exhibit superior performance in charge transport. This unique property arises from their defect-free one-dimensionally confined charge carrier pathway in the direction of $\pi$-$\pi$ stacking, typically along the long-axis of NWs/MWs. Their densely packed $\pi$-conjugated molecular packing along a uniaxial direction is highly beneficial to the efficient charge transport between source and drain electrodes. In addition, they are ideal materials for studying the fundamentals of charge transport due to their high degree of structural perfection (i.e., high crystallinity). Moreover, their large surface-to-volume ratios compared to thin-film counterparts are advantageous in large-scale surface functionalization or chemical modification.

Herein, we report high-performance MW-OPTs using a photo-responsive n-channel organic small molecule, (2Z,2Z)-3,3′-(2,5-dimethoxy-1,4-phenylene)bis(2-(3,5-bis(trifluoromethyl)phenyl)acrylonitrile) (DM-R), as the semiconducting material. The molecular structure is based on distyrylbenzene (DSB) scaffold bearing methoxy (OMe), cyano (CN), and trifluoromethyl (CF$_3$) substituents. It has a nearly coplanar structure through highly ordered $\pi$-$\pi$ stacking, which will be presented (vide infra, crystal structure analysis). Thereby, DM-R is readily self-assembled into a 1-D MW architecture via facile solution processing. The performance of the DM-R MW-OPTs was demonstrated to be superior to that of the DM-R thin-film OPTs by increasing the electron mobility ($\mu_e$) by 59 times, and the photoresponsivity ($R$) by 130 times with stable photoswitching property.
Results and Discussion

Synthesis of DM-R and Fabrication of DM-R MW-OPTs

DM-R was prepared through the Knoevenagel condensation according to the method reported by the Park group.[28] 3,5-Bis(trifluoromethyl)phenylacetoneitrile was treated with 2,5-dimethoxybenzene-1,4-dicarboxaldehyde in tert-butanol. The reaction was activated by the catalytic amount of tetrabutylammonium hydroxide (TBAOH) at 50 °C for 6 h to afford the title compound in a 73% yield (see also Figure 1). It was characterized by 1H nuclear magnetic resonance (NMR, Figure S1) spectrum, matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF), and Fourier transform infrared (FT-IR) spectroscopy (Figure S2 and S3). The formation of DM-R was confirmed by the 1H NMR analysis, showing aromatic and vinyl protons (8.12 and 7.93 ppm), as well as dimethoxy groups (4.01 ppm). Thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses were carried out to reveal the thermal stability and purity of the product (Figure S4). DM-R melts at 302 °C and rapidly decomposes showing its relatively high thermal stability. After the synthesis of DM-R, the prepared material was sublimated using a physical vapor transport (PVT) apparatus to afford high purity. The sublimation temperature of DM-R was 220 °C under a high vacuum condition (~ 10−6 Torr), affording a yield of greater than 60%. DM-R 1-D MWs were fabricated by simple recrystallization, allowing direct crystallization of the molecules in solution phase.

DM-R molecules were easily stacked into 1-D MW structures through π-π stacking interactions. DM-R was dissolved in toluene (0.3 mg/mL) under mild heating at 80 °C. As the solution cooled to room temperature for 2 h, floating DM-R MWs were observed in the solution. The solubility of DM-R in toluene was estimated on the basis of the Beer-Lambert law (Figure S5 and Table S1), revealing the maximum solubility of DM-R 0.35 mM. The solution was vacuum-filtered through a porous anodic aluminum oxide (AAO) membrane. During the filtration, the MWs were washed with an excess of ethyl alcohol to remove residual side products and redispersed in a vial containing pure ethyl alcohol. Figure S6a and S6b show photographs of the DM-R MWs-dispersed toluene solution and the DM-R MWs-redispersed ethanol solution, respectively. Figure 2 shows scanning electron microscopy (SEM) and optical microscope (OM) images of DM-R MWs on the surface of a SiO2/Si wafer. The fabricated MWs exhibited an average diameter of 1.6 ± 0.8 μm and average length of 242.8 ± 133.5 μm. The dark-field optical image of the MW reveals the highly crystalline nature of the MW, as shown in Figure 2c. The transmission electron microscopy (TEM) image is also shown in Figure 2d. Although we performed the selected area electron diffraction (SAED) analysis on the TEM image, the unit cell parameters in the crystal structure were difficult to extract because of damages induced by the electron beam. In addition, single-crystal X-ray diffraction analysis revealed the triclinic P-1 structure of the DM-R MW with a π-planar distance of 3.316 Å (Figure 3 and Table S2, CCDC deposition number: CCDC 1852813).

DM-R MW-OPTs with bottom-gate top-contact configuration were fabricated on a SiO2/Si (300-nm-thick SiO2) wafer using DM-R MWs as the semiconducting layer. To enhance the performance, the surface of SiO2/Si substrates was modified using a self-assembly monolayer (SAM) treatment with n-octadecyltrimethoxysilane (OTS).[28] A DM-R MW dispersion was

![Figure 1. The reaction scheme of DM-R, adapted from reference.[28]](image)

![Figure 2. (a) SEM image of DM-R MW. (b) OM image of DM-R MW. (c) Dark-field OM image of DM-R MW. (d) TEM image of DM-MWs.)](image)

![Figure 3. (a–b) Crystal structure of DM-R MW as (a) view along [100] direction and (b) view along [010] direction. (c) Packing diagram of DM-R MW.](image)
spin-coated onto the OTS-treated SiO₂/Si wafer and the MW-coated wafer was thoroughly dried in a vacuum oven at 80 °C for 12 h. After complete drying, gold electrodes (40 nm) were deposited by thermal evaporation using a shadow mask (channel length ≈ 50 μm). The corresponding OM image and the dark-field image are depicted in Figure S7a and S7b, respectively. For a comparison, DM-R films-based OPTs were also prepared onto OTS-treated SiO₂/Si substrates by thermal evaporation. Ultraviolet-visible (UV–vis) spectra of DM-R thin-film and DM-R MW are illustrated in Figure S8. Due to enhanced electronic coupling between molecules in crystalline solids, the lowest unoccupied molecular orbital (LUMO) levels became lower as the levels of structural perfection increased. The optical band gaps (E_g) of the thin-film and MWs calculated from each long-wavelength absorption edge were 2.31 eV and 1.72 eV, respectively. The MWs showed a relatively broader absorption wavelength region as compared to thin-film. The maximum absorption wavelengths (λ_max) and E_g of DM-R thin-film and MWs are summarized in Table S3.

Optoelectronic Performance of DM-R OPTs

Figure 4a and 4b show schematic images of thin-film-based and MW-based OPTs, respectively. To minimize degradation of the semiconducting layer by oxygen and moisture, the electrical and optoelectronic characteristics of DM-R OPTs were measured in a high vacuum state (under 5.0 × 10⁻⁶ Torr). Typical transfer characteristics (Figure 4c: thin-film OPTs, Figure 4d: MW-OPTs) and output characteristics (Figure 4e: thin-film OPTs, Figure 4f: MW-OPTs) exhibited n-type charge transport behaviors. Moreover, for a more reliable comparison, the transfer characteristics of thin-film and MW-OPTs plotted as current density are also shown in Figure S9. Under optimized conditions, DM-R MW-OPTs showed a two-order of magnitude improvement in maximum μ_s (0.16 cm²V⁻¹s⁻¹) over the DM-R thin-film OPTs (2.7 × 10⁻⁸ cm²V⁻¹s⁻¹), most likely due to the high crystallinity of the self-assembled MW. The inset images show OM images of DM-R thin-film and DM-R MW-OPTs with dark field OM images, revealing the high crystallinity of DM-R MWs. Figure 5a and 5b show transfer characteristics of DM-R thin-film OPTs and DM-R MW-OPTs under dark conditions and light illuminations of peak (460 nm, 510 nm) and valley (410 nm, 560 nm) wavelengths in the light absorption region of DM-R MWs at a drain voltage (V_DS) bias of 10 V. We choose V_GS of 10 V to minimize the MW damage during repeated, long duration measurements. A fixed light intensity (500 μWcm⁻²) was used for the precise comparison of optoelectronic properties of the devices at different wavelengths. Under irradiation conditions, the on- and off-currents of transistors increased due to the generation of photocurrent (I_ph). The threshold voltage (V_T) was also shifted negatively with the easy turn-on of device. This result was attributed to the decreased number of trap sites by photogenerated charge carriers in DM-R. The increases in drain current (I_D) under light illumination were well matched with the DM-R absorption characteristic. Illumination of light with a 460 nm wavelength showed the largest increase in I_D, as the wavelength matched well with the λ_max of both DM-R thin-film and MW (see Figure S8).

The optoelectronic properties of DM-R, photoresponsivity (R) and photocurrent/dark-current ratio (P) of DM-R OPTs were obtained from I–V (transfer) characteristics by following equations:¹⁻¹⁻¹

\[
R = \frac{I_{ph}}{P_{inc}} = \frac{I_{light} - I_{dark}}{P_{inc}}
\]

(1)

\[
P = \frac{I_{light} - I_{dark}}{I_{dark}}
\]

(2)

where I_ph is the photocurrent, I_light and I_dark are I_D under illumination and in the dark, respectively, and P_inc is the incident illumination power on the channel of the device. In addition, the external quantum efficiencies (EQEs) of DM-R OPTs were also calculated from the transfer characteristics. Usually, EQE is defined as the ratio of the number of photogenerated carriers that enhance the I_D to the number of photons incident on the channel area. The EQE is expressed by the following equation:
EQE = \frac{(I_{\text{light}} - I_{\text{dark}})hc}{\varepsilon P \mu \lambda}

where $h$ is the Planck constant, $c$ the speed of light, $\varepsilon$ the fundamental unit of charge, $P_{\text{int}}$ the incident light intensity, $A$ the area of the transistor channel, and $\lambda$ the peak wavelength of the incident light, respectively.

Figure 5c, 5e, and 5g show the $R$, $EQE$, and $P$ values of thin-film and MW-OPTs for: (c,e,g) as a function of $V_G$ or (d,f,h) as a function of wavelength of illuminated light (500–785 nm) at $V_G = 80$ V.

Overall, the DM-R MW-OPTs showed much higher $R$ and $EQE$ values than those of DM-R thin-film OPTs at the studied wavelengths. At a wavelength of 460 nm, the $R$ and $EQE$ values of MW-OPTs (23.53 A W$^{-1}$ and 6348.4%, respectively) were approximately 130 times higher than those of thin-film OPTs (0.18 A W$^{-1}$ and 47.6%, respectively). This superior outcome together with the observation of photomultiplication in MW-OPTs was due to the single crystalline nature, the long exciton diffusion length and the enhanced absorptivity of the MWs.[32]

In DM-R MW-OPTs, photoexcitation can cause a high density of accumulated holes at the semiconductor/electrode interface, and then tunneling phenomenon of electrons may result in photomultiplication, similarly to other organic phototransistors and photodiodes.[1,33–35] In addition, the single-crystalline nature of the MW enables the fast supply of photogenerated charge carriers to the semiconductor/electrode and semiconductor/dielectric interface, leading to the effectively filling of charge traps and higher mobility.[22] Moreover, multiple exciton generation phenomenon may also contribute to photomultiplication to some degree.[36] In addition, the lower $E_g$ of MWs (1.72 eV) compared to thin-films (2.31 eV) caused an increased number of photons to be absorbed by the irradiated light, yielding a higher $EQE$ value in the DM-R MW-OPTs.[37] At a wavelength of 460 nm, both thin-film OPTs and MW-OPTs exhibited higher performances than other wavelengths, which was also consistent with the optimal absorption ranges of both DM-R thin-films and MWs. On the other hand, the $P$-value of the thin-film OPTs at 460 nm was 1.5, which was larger than that (0.5) of the MW-OPTs at the same wavelength. The key parameters of OPTs are summarized in Table 1.

**Table 1.** Device characteristics of DM-R thin-film and MW-OPTs at $V_G$ of 80 V at a fixed light intensity of 500 μW cm$^{-2}$.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>$R$ (A W$^{-1}$)</th>
<th>$EQE$ (%)</th>
<th>$P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>410</td>
<td>0.14</td>
<td>41.6</td>
<td>1.1</td>
</tr>
<tr>
<td>Thin-film</td>
<td>13.33</td>
<td>4035.7</td>
<td>0.3</td>
</tr>
<tr>
<td>460</td>
<td>0.18</td>
<td>47.6</td>
<td>1.5</td>
</tr>
<tr>
<td>MW</td>
<td>23.53</td>
<td>6348.4</td>
<td>0.5</td>
</tr>
<tr>
<td>510</td>
<td>0.16</td>
<td>39.5</td>
<td>1.4</td>
</tr>
<tr>
<td>Thin-film</td>
<td>13.61</td>
<td>3311.0</td>
<td>0.3</td>
</tr>
<tr>
<td>560</td>
<td>0.07</td>
<td>15.0</td>
<td>0.6</td>
</tr>
<tr>
<td>MW</td>
<td>8.71</td>
<td>1965.8</td>
<td>0.2</td>
</tr>
</tbody>
</table>
On/off switching Behaviors and Charge Accumulation/release Rates

The photoresponse characteristics of DM-R thin-film OPTs and MW-OPTs were investigated through measuring the photo-on/off switching behaviors under external light with wavelength of 460 nm (blue). The $I_{ph}$ of the DM-R thin-film OPTs (Figure 6a) and DM-R MW-OPTs (Figure 6b) were plotted as a function of time in their transistor off-state ($V_{GS} = 0$ V, $V_{DS} = 10$ V). Under illumination, the photogenerated charge carriers in the DM-R thin-film and DM-R MW significantly increased, resulting in an increased $I_{ph}$. Both the thin-film and MW-OPTs showed charging characteristics that were often observed from OPTs [22,28-42] and these charging characteristics might be caused by charge (electron) trapping by the OCH groups in DM-R. The normalized on-state current density of DM-R MW-OPTs ($7.2 \times 10^{-7}$ A mm$^{-2}$) was ~10 times higher than that of DM-R thin-film OPTs ($7.0 \times 10^{-8}$ A mm$^{-2}$). The enhanced photoconductivity and light sensitivity of DM-R MWs over the thin-film may be attributed to the more efficient charge transport properties induced by the π-stacked MW structure. For further investigation of charge carrier dynamics of the DM-R thin-film and MW, the charge accumulation and release rates were calculated from the selected regions in Figure 6a and b. A specific trend of charge accumulation and release was observed at the initial stage of turn-on and turn-off of light. The charge accumulation and release rates from deep traps can be parsed from modifying the conventional transistor equation in the saturation regime [22,43]

$$\text{rate} = \frac{dQ}{dt} = \frac{C}{LW} \frac{dV_C(t)}{dt} = \frac{2C}{\mu_{sat}W} \left( \frac{d(I_{ph}(t))^{1/2}}{dt} \right)^{1/2}$$

In this equation, $Q$ is the amount of charge carriers, $C$ is the insulator capacitance per unit area, $L$ and $W$ are the channel length and width, respectively, and $\mu_{sat}$ is the saturation regime mobility. The corresponding charge accumulation (Figure 7a) and release rates (Figure 7b) were calculated by applying equation (4) and a least-squares linear fit to the raw data. The charge accumulation rates in the DM-R thin-film OPTs and DM-R MW-OPTs were found to be $1.14 \times 10^{13}$ cm$^{-2}$ s$^{-1}$ (Region A in Figure 6a) and $6.88 \times 10^{13}$ cm$^{-2}$ s$^{-1}$ (Region C in Figure 6b), respectively. The charge release rate of DM-R MW-OPTs was found to be $4.57 \times 10^{12}$ cm$^{-2}$ s$^{-1}$ (Region D in Figure 6b), which is slightly lower than its charge accumulation rate. In the case of DM-R thin-film OPTs, the charge release rate was calculated from the initial and stabilized regions (Region B in Figure 6a). At the initial region, the charge release rate ($1.11 \times 10^{13}$ cm$^{-2}$ s$^{-1}$) was much faster than the stabilized region ($5.83 \times 10^{13}$ cm$^{-2}$ s$^{-1}$). In both regions, the charge release rates of DM-R thin-film OPTs were higher than those of DM-R MW-OPTs, indicating a faster charge releasing process.

After turn-off the light, the $I_{ph}$ decreased in one step in DM-R MW-OPTs. On the other hand, two-step decrease was observed in the DM-R thin-film OPTs, indicating an initial rapid charge decay process followed by a secondary stabilized decay process. For the details of $I_{ph}$ decay dynamics, we further investigated the charge decay process of DM-R thin-film OPTs and DM-R MW-OPTs, as shown in Figure 7c. The charge decay curves of the $I_{ph}$ in the transistor off-state can be described by:

$$l(t) = l_{dark} + A[\exp(-t/\tau_1)]$$

$$l(t) = l_{dark} + A[\exp(-t/\tau_1)] + B[\exp(-t/\tau_2)]$$

where $t$ is time, $\tau_1$ and $\tau_2$ are time constants, $l_{dark}$ is the dark current, and $A$ and $B$ are scaling constants. Equation (5) shows the mono-exponential decay behavior with single charge time constant ($\tau_1$), whereas equation (6) shows the second-order decay behavior with two charge quenching time constants ($\tau_1$ and $\tau_2$). By fitting the $I_{ph}$ data of DM-R MW-OPTs with exponential decay behavior to the first order decay equation (5), and the thin-film to the second order decay equation (6), we obtained each material’s charge quenching time constant. For the DM-R MW-OPTs, the $I_{ph}$ decay dynamics followed a first order decay process with a charge quenching time constant of $\tau_1 = 10.7$ s. The DM-R thin-film OPTs’ $I_{ph}$ decay dynamics followed the second order decay process, with a charge quenching time constant of $\tau_1 = 2.5$ s for the initial step and $\tau_2 = 14.1$ s for secondary charge quenching. The charge quenching time constant for DM-R thin-film OPTs at initial time (2.5 s) was shorter than the time constant of DM-R MW-OPTs (10.7 s), indicating that a longer charge relaxation time is needed for MW than for DM-R thin-film OPTs. The second order $I_{ph}$ decay of DM-R thin-film OPTs is most likely due to their many trap sites present in the amorphous structure.
Conclusions

The work described here provides an efficient solution-based approach for obtaining a 1-D MW assembly for high-performance n-type OPTs. We synthesized a highly photo-sensitive DM-R organic small molecule by the Knoevenagel condensation, and fabricated DM-R MWs by a simple solution-based recrystallization method. The electrical and optoelectronic properties of DM-R MW-OPTs were quantitatively investigated in comparison with those of DM-R thin-film OPTs. It was found that DM-R MW-OPTs have superior photo-responsive properties, due to their structural perfection. The DM-R MW-OPTs exhibited highly enhanced $\mu_n$ (0.16 cm$^2$ V$^{-1}$ s$^{-1}$) compared to that of the DM-R thin-film OPTs (2.7 $\times$ 10$^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$). Moreover, the $R$ (23.53 A W$^{-1}$) and $\text{EQE}$ (6348.4%) values of MW-OPTs at 460 nm showed a 130-fold enhancement compared to DM-R thin-film OPTs due to the highly crystalline structure of their MWs. Furthermore, the stable photo-on/off switching behaviors of DM-R MW-OPTs and DM-R thin-film OPTs revealed that DM-R MW-OPTs exhibited the faster charge accumulation and slower charge release rates (6.68 $\times$ 10$^{-3}$ cm$^2$ s$^{-1}$, 4.57 $\times$ 10$^{-3}$ cm$^2$ s$^{-1}$, respectively) than those of DM-R thin-film OPTs (1.14 $\times$ 10$^{-3}$ cm$^2$ s$^{-1}$, 5.83 $\times$ 10$^{-3}$ cm$^2$ s$^{-1}$, respectively). Our developed DM-R MWs will contribute to the development of high-performance optoelectronic devices that exhibit enhanced n-channel charge transport properties, a high light responsivity, and improved multiplication of the photoinduced current.

Experimental Section

Synthesis and Characterization of DM-R and DM-R MWs

2,5-dimethoxybenezene-1,4-dicarboxaldehyde (100 mg, 0.515 mmol, 1 equiv) and 3,5-bis(trifluoromethyl)phenylacetonitrile (266 mg, 1.05 mmol, 2 equiv) were dissolved in anhydrous tert-butanol (5 mL). A catalytic amount of TBAOH (10 mg) was slowly dropped into the mixture and stirred at 50 °C for 6 h. The resulting precipitate was filtered and washed with isopropanol to afford a yellow powder (250 mg, 0.376 mmol, 73%). Vacuum sublimation was conducted for further purification. m.p. = 302 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.12 (s, 6H), 7.93 (s, 4H), 4.01 (s, 6H); m/z (MALDI-TOF) calcd. for C$_9$H$_9$F$_3$N$_2$O$_4$ [M$^+$] 664.10, measured 664.03; FT-IR (ATR) 2214 cm$^{-1}$ (C=N stretching vibration). After the synthesis of DM-R, the as-prepared material was sublimated using a PVT apparatus to afford high purity. The sublimation temperature of DM-R was 220 °C and its yield was over 60%. DM-R was dissolved in toluene, with a concentration of 0.3 mg mL$^{-1}$ under mild heating at 80 °C. As the solution cooled to room temperature for 2 h, floating DM-R MWs were observed in the solution. The solution was vacuum-filtered with a porous AAO membrane (pore diameter $\approx$ 0.22 μm). During the filtration, the MWs were washed with an excess of ethyl alcohol to remove residual reagents, and dispersed in a vial containing pure ethyl alcohol. A $^1$H NMR spectrum was recorded on an Agilent 400-MR DD2 instrument. MALDI-TOF spectrum was recorded on a Bruker Ultraflex III instrument. FT-IR spectrum was recorded on a Thermo Scientific Nicolet iR200 FT-IR instrument. TG-DSC analyses were conducted on a TA Instruments SDT Q600. UV-vis absorption spectra were measured on a Cary 5000 spectrophotometer and Shimadzu UV-1800. The SEM images were obtained using a Hitachi cold SEM microscope, and the TEM images were obtained using a JEM-2100 instrument (JEOL) operated at 200 kV. The single-crystal X-ray diffraction data were collected with Mo K$_\alpha$ radiation at 173 K using a Rigaku R-Axis Rapid II. The Rapid Auto software (Rapid Auto software, R-Axis series, Cat. No. 9220810, Rigaku Corporation) was used for data collection and processing. The crystal structure was solved by the direct method and refined by full-matrix least-squares calculations using the SHELXTL program package.[46] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were located at geometrically calculated positions. Crystal data are summarized in Tables S2.

Surface Modification of Substrate

Heavily n-doped Si wafers (<0.004 Ω cm) with a 300 nm-thick SiO$_2$, dielectric (C$_{18}$-11.5 nF cm$^{-2}$) were used as the substrate for OPTs. The surface of Si wafer was treated with OTS in a solution phase.[45] Wafers were first cleaned by piranha solution (70:30 H$_2$SO$_4$:H$_2$O$_2$ by vol%) for 20 min and rinsed in deionized (DI) water, followed by nitrogen gun blowing. The SiO$_2$/Si substrates were consecutively treated with UV-ozone plasma for 15 min. For OTS treatment, the cleaned substrates were spin-coated with a 3 mM solution of OTS in trichloroethylene and then placed in a desiccator under vaporized ammonium hydroxide for 12 h at room temperature. The modified substrates were ultrasonicated with toluene and rinsed sequentially with toluene, acetone and isopropyl alcohol, followed by drying with nitrogen gun blowing.

Fabrication and Characterization of OPTs

DM-R MW dispersion was spin-coated onto the OTS-treated SiO$_2$/Si wafer at 700 rpm for 7 s, followed by 3.000 rpm for 10 s. The MW-coated wafer was then thoroughly dried in a vacuum oven at 80 °C for 12 h. After complete drying, gold electrodes (40 nm) were deposited by thermal evaporation using a shadow mask (channel length $\approx$ 50 μm, channel width $\approx$ 1.000 μm). For comparison, thermally evaporated DM-R films (50 nm) were prepared onto OTS-treated SiO$_2$/Si substrates kept at 65 °C under high vacuum (<5.0 × 10$^{-6}$ Torr). Gold electrodes (40 nm) were thermally evaporated using a shadow mask to form DM-R thin-film OPTs. The I–V and on/off photoswitching characteristics of the devices were measured in a high vacuum condition (under 5.0 × 10$^{-3}$ Torr) using a Keithley 4200 semiconductor parametric analyzer. The $\mu_n$ was calculated in the saturation regime using the following equation:

$$I_o = \frac{W}{2L} \mu_n (V_G - V_I)^2$$

Special Issue footnote

This manuscript is part of a special issue on Organic Materials. A link to the Table of Contents of the special issue will appear here when the complete issue is published.

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Conflict of Interest

The authors declare no conflict of interest.

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