Thermal and Optical Modulation of the Carrier Mobility in OTFTs Based on an Azo-anthracene Liquid Crystal Organic Semiconductor

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Supporting Information

ABSTRACT: One of the most striking features of organic semiconductors compared with their corresponding inorganic counterparts is their molecular diversity. The major challenge in organic semiconductor material technology is creating molecular structural motifs to develop multifunctional materials in order to achieve the desired functionalities yet to optimize the specific device performance. Azo-compounds, because of their special photoresponsive property, have attracted extensive interest in photonic and optoelectronic applications; if incorporated wisely in the organic semiconductor groups, they can be innovatively utilized in advanced smart electronic applications, where thermal and photo modulation is applied to tune the electronic properties. On the basis of this aspiration, a novel azo-functionalized liquid crystal semiconductor material, \((E)-1-(4-(anthracen-2-yl)phenyl)-2-(4-(decyloxy)phenyl)diazene (APDPD),\) is designed and synthesized for application in organic thin-film transistors (OTFTs). The UV–vis spectra of APDPD exhibit reversible photoisomerization upon photoexcitation, and the thin films of APDPD show a long-range orientational order based on its liquid crystal phase. The performance of OTFTs based on this material as well as the effects of thermal treatment and UV-irradiation on mobility are investigated. The molecular structure, stability of the material, and morphology of the thin films are characterized by thermal gravimetric analysis (TGA), polarizing optical microscopy (POM), (differential) scanning calorimetry (DSC), UV–vis spectroscopy, atomic force microscopy (AFM), and scanning tunneling microscopy (STM). This study reveals that our new material has the potential to be applied in optical sensors, memories, logic circuits, and functional switches.

KEYWORDS: photoresponsive, azo-compound, liquid crystal, anthracene, organic thin-film transistors

1. INTRODUCTION

Owing to the wide applications of organic thin-film transistors (OTFTs) in integrated circuits, active matrix displays, flexible displays, and sensors, organic semiconductors have attracted much attention over the past two decades.1,2 Compared with inorganic thin-film transistors based on Si, OTFTs possess many appealing advantages such as easy and diverse modifications of the organic molecular structures, simple and low-cost fabrication approaches, and flexibility.3,4 As such, various synthetic strategy methods and structure–property studies have been devoted to design organic functional semiconductor materials with the goal to achieve high carrier mobility, good environmental stability, and optimized specific device performance.5–7 Among numerous semiconductor materials, acenes have shown excellent performance because of their strong intermolecular overlap stemming from the stable and powerful \(\pi–\pi^*\) conjugated system.9,9 However, the stability of this class of organic semiconductors is not as good as expected, such as pentacene and its derivatives.10,11 To realize commercial applications, the conjugated core moiety has been shortened for lowering the highest occupied molecular orbital (HOMO) in order to overcome the instability problem.12,13 Various anthracene derivatives have been investigated and reported. In all cases, these anthracene-based organic semiconductors showed improved stability with relatively good device performance.14,15 Particularly, a recently reported anthracene semiconductor material with a phenyl group covalently attached to the anthracene core exhibited extended \(\pi–\pi^*\) conjugated properties and demonstrated remarkably high carrier mobility, >10 cm² V⁻¹ s⁻¹.16 On the other hand, research efforts have been devoted to the synthesis of new materials with tunable optical and electronic
transport ability is improved. These photochromic molecules, however, are mostly applied as a dielectric layer or doped into the semiconductor layer and are rarely used directly as the active layer in OTFTs. A simple way to implement a multifunctional OTFT semiconductor material in a device is an attractive strategy. Azobenzene chromophore, a kind of photochromic molecule, has been demonstrated with outstanding photoisomerization features due to their reversible conformational changes in response to photoexcitation. They possess wide applications including reversible phase-transfer nanoparticles, light-controlled switches, and photoresponsive self-assembly vesicles. Generally, azo-compounds always exist in the cis-form, which is thermodynamically stable under natural conditions and will convert to cis-form under UV-irradiation of proper wavelength. The inverse process, from cis-form to trans-form, emerges upon visible light exposure or heat treatment. Previous studies have revealed that OTFTs based on directly deposited azobenzene molecules, as active layer, show low mobility and poor stability. We proposed the design and synthesis of a novel azo-functionalized OTFT material by attaching the azobenzene unit to an anthracene core to balance the charge mobility and photochromic performance.

Previous research has demonstrated that a highly ordered liquid crystal phase can abet the organic semiconductor molecule to arrange in a better orientation so that the carrier liquid crystal phase can abet the organic semiconductor chromic performance.

Scheme 1. Synthetic Routes of APDPD

Materials. All the reagents and solvents purchased were used without further purification except as otherwise mentioned. The synthetic routes are shown in Scheme 1. 2-Bromoanthracene (2), 2-anthraceneborate (3), 1-(decyloxy)-4-nitrobenzene (5), 4-(decyloxy)-aniline (6), and (E)-4-((4-(decyloxy)phenyl)diazenyl)phenol (7) were prepared according to the literature procedures.

Synthesis. Preparation of (E)-4-((4-(Decyloxy)phenyl)diazenyl)-phenyl Trifluoromethanesulfonate (8). A 250 mL flask containing (E)-4-((4-(decyloxy)phenyl)diazenyl)phenol (19.35 mmol) was equipped with a magnetic bar and protected by N2. Then 100 mL of dry dichloromethane and 8.05 mL of triethylamine were added, and the solution was cooled to −20 °C. After that, 4.84 mL of triflic anhydride was added by dripping slowly with a syringe. The reaction mixture was allowed to warm up to room temperature after stirring at −20 °C for 1.5 h. After reaction, 100 mL of dichloromethane was added to the mixture before it was washed with 100 mL of water and 100 mL of brine, three times for both. The organic layer was dried over Na2SO4, and the solvent was removed by evaporation under reduced pressure. Then the crude product was purified through silica gel column chromatography (petroleum ether/dichloromethane = 4/1), and 7 g of pure material was obtained as an orange solid with a yield of 75%. H NMR (300 MHz, CDCl3) δ 7.99−7.87 (m, 4H), 7.40 (d, J = 9.0 Hz, 2H), 7.01 (d, J = 9.0 Hz, 2H), 4.05 (t, J = 6.6 Hz, 2H), 1.88−1.77 (m, 2H), 1.51−1.23 (m, 14H), 0.88 (s, J = 6.7 Hz, 3H). 13C NMR (75 MHz, CDCl3) δ 162.50 (s), 152.13 (s), 150.36 (s), 146.73 (s), 125.29 (s), 124.38 (s), 118.90 (q, Jc=320.9 Hz), 114.96 (s), 68.60 (s), 32.05 (s), 29.70 (s), 29.52 (s), 29.47 (s), 29.31 (s), 26.15 (s), 22.83 (s), 14.26 (s). H NMR spectrum and 13C NMR spectrum are shown in Figures S1 and S2.

Preparation of (E)-1-((4-Anthracen-2-yl)phenyl)-2-(4-(decyloxy)phenyl)diaze (9). A 100 mL pressure bottle containing (E)-4-((4-
In our research, a new semiconductor material, APDPD, with both thermal and photochromic properties, is synthesized and investigated. The UV−vis spectra of APDPD in dichloromethane show variations after frequent treatment with UV-irradiation and heating. The optical and electrochemical characterizations of APDPD were carried out using UV−vis absorption, cyclic voltammetry, and electrochemical impedance spectroscopy (EIS).

The UV−vis spectra of APDPD in solution and as a thin film show characteristic absorptions at 449 nm in solution and 459 nm in thin films, indicating a relatively shallow energy gap of 2.76 eV. The photoluminescence (PL) spectra of the thin films show a broad emission peak at 560 nm, corresponding to the lowest unoccupied molecular orbital (LUMO) level. The detailed optical and electrochemical properties of APDPD are summarized in Table 1.

Furthermore, we also studied the electrochemical characteristics of APDPD by cyclic voltammetry. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels were determined using cyclic voltammetry. The HOMO level was calculated to be 2.70 eV, while the LUMO level was found to be 5.98 eV. These values are consistent with the DFT calculations (Figure 2b). The electron and hole mobilities were measured using four-point probe measurements and were found to be 0.03 cm²/Vs and 0.02 cm²/Vs, respectively.

Figure 1. (a) UV−vis spectra of APDPD in dichloromethane (CH₂Cl₂) under repetitive UV irradiation for 1 min and then exposure to visible light for 130 s (black arrows represent variation tendency of UV-irradiation and red arrows represent variation tendency of visible light irradiation). (b) UV−vis spectra of APDPD thin films on quartz (black line) and solution in dichloromethane (CH₂Cl₂) (red line). (c) Cyclic voltammetry of APDPD thin films on the glassy carbon electrode (GCE) (Φ = 3 mm) in CH₂Cl₂/TBAPF₆ (tetrabutylammonium hexafluorophosphate) solution.

(dicycloxyphenyl)di[a]zoyl]phenyl trifluoromethanesulfonate (4 mmol), 2-anthraceneborate (4.4 mmol), and Pd(PPh₃)₄ (0.2 mmol) was filled with N₂ for 15 min, and then was added 8 mL of ethanol, 32 mL of toluene, and 8 mL of 2 M K₂CO₃ aqueous solution sequentially. The mixture was heated overnight. When the reaction was finished, the whole system was filtered and the filtrate was collected to be washed with water, ethanol, and acetonitrile successively and cautiously. The dried crude product was further purified by sublimation through a 5-zone furnace with a vacuum degree of 10⁻³ Pa and heating temperatures of 260, 220, 180, 140, and 80 °C, respectively (Figure S3). Finally, 1.4 g of pure material was obtained as an orange solid with a yield of 70%.

Because of the low solubility of APDPD, we could not obtain its ¹H NMR data; instead, we select the high-resolution mass spectrum, which is provided in Figure S4, and elemental analysis (calculated for C₃₆H₃₈N₂O: C, 84.01; H, 7.44; N, 5.44. Measured: C, 84.12; H, 7.41; N, 5.34) to confirm the structure of APDPD.

Device Fabrication. The OTFT devices with bottom-gate, top-contact structures were fabricated by vacuum-deposition on the heavily doped silicon wafers with predeposited 300 nm silicon dioxide layer. Before use, the silicon wafers with silicon dioxide coating were washed with acetone, deionized water, and isopropanol in ultrasonic cleaner. The contact structures were fabricated by vacuum-deposition on the heavily doped silicon wafers with predeposited 300 nm silicon dioxide layer. After that the mixed solution was set to 90 °C for 30 min, successively. After that the silicon wafers were placed under acetone, deionized water, and isopropanol in ultrasonic cleaner.

3. RESULTS AND DISCUSSION

In our research, a new semiconductor material, APDPD, with both thermal and photochromic properties, is synthesized and investigated. The UV−vis spectra of APDPD in dichloromethane show variations after frequent treatment with UV-irradiation (with a handheld UV lamp of 6 W and 254 nm), heating, and visible light irradiation. The reversible isomerization of trans−cis−trans can be observed in the UV−vis spectra (Figure 1a). The intensity of the absorption peak at λmax = 365 nm decreases and the edge segments of the spectrum increase slightly under UV-irradiation until a photostationary state appears, representing the transformation from trans-form to cis-form. The reverse process emerges with the original spectrum reverting to another photostationary state under visible light irradiation or heat treatment, which represents the cis-form converting back into trans-form. Because of the compact molecular packing, the isomerization process in the solid state requires more time than that in the solution and is not very obvious (Figure S5). In addition, the onset absorption wavelengths are found to be 449 nm in solution and 459 nm in thin film on quartz (Figures 1b and S6). According to the UV−vis spectra of the thin film, the optical band gap is calculated to be 2.70 eV. The photoluminescence (PL) spectra of the material (APDPD) in solution and as a thin film were obtained, but the results show that APDPD is not luminescent like other anthracene-based semiconductors.

Furthermore, we also studied the electrochemical characteristics of APDPD by cyclic voltammetry. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels were determined using cyclic voltammetry. The HOMO level was calculated to be 2.70 eV, while the LUMO level was found to be 5.98 eV, but it does not match well with the Au electrode (work function 5.1 eV). Therefore, the carrier mobility of the OTFTs based on APDPD can be improved if the energy barrier is reduced by further modification in the device structure. The frontier molecular orbitals for APDPD were calculated by density functional theory (DFT) using B3LYP functional analysis and 6-311G(d,p) basis set with Gaussian 09 package (Figure 2a). Besides that, the scanning tunneling microscopy (STM) constant-height dI/dV mappings of both negative bias and positive bias operation represent the HOMO and LUMO levels, which are consistent with the DFT calculations (Figure 2b). It is obvious from both DFT calculations and dI/dV mappings of STM that the electron distribution mostly locates in anthracene at the HOMO level, while it moves to the azobenzene group at the LUMO level. The detailed optical and electrochemical properties are summarized in Table 1.
Figure 2. (a) Frontier molecular orbitals for APDPD calculated by DFT (B3LYP/6-311G(dp) level). (b) dl/dV mapping of scanning tunneling microscopy (STM) under constant-height mode.

Table 1. Optical and Electrochemical Properties of APDPD

<table>
<thead>
<tr>
<th>UV–vis (nm)</th>
<th>CV (V)</th>
<th>CV (eV)</th>
<th>UV–vis (eV)</th>
<th>calculation</th>
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<td></td>
</tr>
<tr>
<td>APDPD</td>
<td>449</td>
<td>459</td>
<td>−1.88</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>459</td>
<td>459</td>
<td>−3.22</td>
<td>−5.98</td>
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<td></td>
<td>459</td>
<td>459</td>
<td>−5.42</td>
<td>3.07</td>
</tr>
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</table>

“Solution and film absorption edge.” †Electrochemical reduction and oxidation potential determined versus Fc/Fc+.*E_{LUMO} = (E_{HOMO} + 5.1) E_{LUMO} = (E_{HOMO} + 5.1).  E_{LUMO} = E_{HOMO} − E_{HOMO}.  Optical band gap estimated from the absorption edge of the solution and thin film.  Calculated by DFT (B3LYP/6-311G(dp) level).
compared with that of the thin film at 200 °C, some cracks are observed in the (DSC), and (c) polarizing optical microscope (POM) images during the cooling process. The calculations for only be observed in a small region on the thin package. Moreover, because monolayer molecular packing can be seen that the surface morphology changes obviously after annealing at 100, 150, and 200 °C. After annealing at 100 °C, the worm-shaped grains aggregate together to form bigger rodlike structures without terraces and possess a disoriented arrangement (Figure 5a2), which is unfavorable to the molecular stacking and results in a decreased device mobility compared with that of the devices at RT. When the annealing temperature is raised up to 150 and 200 °C, the material achieves highly ordered liquid crystal phase (SmX) so that the molecules are able to realign, and after cooling naturally to room temperature they rearrange to form larger grain sizes without any worm-shaped grains, thus resulting in a smooth, plain, and uniform film that deserves a better charge-transport property (Figure 5a3 and a4). Although the thin films annealed at both 150 and 200 °C possess the same liquid crystal phase (SmX), some cracks are observed in the film with the rise in the temperature at 200 °C, which leads to a bit lower mobility compared with that of the thin films annealed at 150 °C (Figure 5a4).

The cross section curves and detailed values of steps at 150 and 200 °C are shown in Figure 5a5 and a6, respectively, whereas the thin films at RT and 100 °C do not have any obvious steps. The height of the terraces is measured to be 6.5 nm on average, which is approximately twice the molecular length (3.53–3.55 nm) calculated with the help of Multiwfn (version 3.3.9) (Figure 5a),39 which indicates the molecular packing structure (Figure S10).27,40 The calculations for molecular structure were carried out by density functional theory (DFT) using hybrid B3LYP functional with 6-311G-(d,p) basis set for geometrical optimization and single point energy, and all the calculations were performed in Gaussian 09 package. Moreover, because monolayer molecular packing can only be observed in a small region on the thin film annealed at 150 °C, it may be concluded that molecules are mostly arranged in bilayers (Figure S11). After UV-irradiation of all the thin films for 1 h, through in situ measurements it is interestingly found that only the thin films without annealing (RT) are slightly changed, with the growth in size of superficial grains along their width while keeping the same shape (Figure 5a1 and b1). It can be seen that morphologies of the three thin films are almost unchanged (Figure 5a2 and b2, a3 and b3, and a4 and b4). The height of the terraces still remains ~6.6 nm after UV-irradiation of the thin films annealed at 150 and 200 °C (Figure 5b5 and b6), and little differences in the morphology are not able to demonstrate the high performance of corresponding OTFT devices after UV-irradiation.

A comparison of the XRD patterns of the thin films at RT, annealed at 100, 150, and 200 °C and UV-irradiated, is shown in Figure 6b. The XRD patterns demonstrate the crystallinity and orientation of the molecules exactly in accordance with the morphology of the thin films shown by AFM images and the device performance. For all five different treatment methods, we can see four diffraction peaks, but the significant difference of the intensity can only be seen in the first peak, as compared with the XRD pattern of the thin films at RT. In detail, at the annealing temperature of 100 °C, the thermal energy just facilitates the molecular grains to aggregate physically (as seen in the AFM images), and this process disturbs the molecular arrangement; thus, the intensities of all diffraction peaks become weaker. When the annealing temperature goes up to 150 °C, the molecules attain a highly ordered liquid crystal phase (SmX) and realign to form an ordered orientation with high crystallinity; therefore, the first peak possesses dramatically high intensity. Although at 200 °C it is still in the liquid crystal phase (SmX), the relatively high temperature makes the film slightly crack, affecting the ordered arrangement and crystallinity of the molecules to some extent. The appearance of a fifth peak upon annealing at 150 and 200 °C also indicates that the molecules are rearranged in a highly ordered alignment.

![Figure 3. Thermal properties and optical textures of APDPD. (a) Thermal gravity analysis (TGA), (b) differential scanning calorimetry analysis (DSC), and (c) polarizing optical microscope (POM) images during the cooling process.](image-url)
within their liquid crystal phase. The intensity of the peaks, especially the first peak, increases after UV-irradiation, which demonstrates the enhancement of crystallinity and molecular alignment.

Scanning tunneling micrographs of self-assembled monolayers of azo-liquid crystal compound APDPD on gold surface were obtained to investigate its photoisomerization and subtle structure. Upon deposition at low APDPD concentration, STM observations directly show well-ordered molecular arrangement on Au(111). As illustrated in Figure 7a and b, fishbone-shaped molecular features are mostly assembled at the elbow sites of Au(111), which induce the same orientation of most of the molecular self-assembled structural units. The high-resolution STM image in Figure 7c reveals the clear structure of individual APDPD molecules within the fishbone-shaped supramolecular structures. The stripe comprised of three different linking
structures is in good agreement with the structure of APDPD. The molecular length is measured to be \( \sim 3.3 \) nm, which is very close to the value of \( 3.53 - 3.55 \) nm obtained by calculations. Figure 7d exhibits the STM manipulation process in which the lateral stripe was pulled out and put back to further confirm that each stripe represents an APDPD molecule. The molecular layer was treated with electron excitation instead of UV-irradiation to explore the isomerization from trans-form to cis-form for their same essence. However, the photoisomerization failed through the STM experiment on monomolecular layer because the molecule–surface coupling quenched the process. The mechanism of quenching has been demonstrated as follows: (i) Electronic lifetime effects: the time of a whole molecular conformational changing process is longer than the lifetime of the excited electron acting on the surface. (ii) Substrate-induced changes in optical absorption: the optical absorption is changed and then affects the photoswitching process because of the hybridization between molecules and substrate. In addition to this, the dramatically increased mobility of OTFT devices after UV-irradiation may be attributed to the synergistic effects of photoisomerization and

## Table 2. OTFT Devices Performance of APDPD with Different Treatment Process

<table>
<thead>
<tr>
<th>material</th>
<th>annealing temp (°C)</th>
<th>UV-irradiation (254 nm)</th>
<th>( \mu_{\text{avg}} ) (cm(^2) V(^{-1}) s(^{-1}))</th>
<th>( \mu_{\text{max}} ) (cm(^2) V(^{-1}) s(^{-1}))</th>
<th>( V_{\text{th}} ) (V)</th>
<th>( I_{\text{on}}/I_{\text{off}} )</th>
</tr>
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<tbody>
<tr>
<td>RT</td>
<td></td>
<td></td>
<td>0.042</td>
<td>0.047</td>
<td>-52.0</td>
<td>2.0 ( \times 10^4 )</td>
</tr>
<tr>
<td>100</td>
<td></td>
<td></td>
<td>0.019</td>
<td>0.024</td>
<td>-53.6</td>
<td>1.1 ( \times 10^4 )</td>
</tr>
<tr>
<td>150</td>
<td></td>
<td></td>
<td>0.229</td>
<td>0.302</td>
<td>-52.1</td>
<td>1.8 ( \times 10^5 )</td>
</tr>
<tr>
<td>200</td>
<td></td>
<td></td>
<td>0.115</td>
<td>0.179</td>
<td>-51.4</td>
<td>1.1 ( \times 10^5 )</td>
</tr>
<tr>
<td>APDPD</td>
<td>RT</td>
<td></td>
<td>0.285</td>
<td>0.359</td>
<td>-41.1</td>
<td>6.1 ( \times 10^5 )</td>
</tr>
<tr>
<td>100</td>
<td>1 h</td>
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<td>0.105</td>
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<td>150</td>
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<tr>
<td>200</td>
<td>1 h</td>
<td></td>
<td>0.474</td>
<td>0.602</td>
<td>-45.8</td>
<td>1.1 ( \times 10^6 )</td>
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</table>

Figure 5. Normal AFM images of APDPD thin films fabricated on the OTS-treated SiO\(_2\)/Si substrate with two series: (a1–a4) at RT and thermal annealing at 100, 150, and 200 °C and (b1–b4) UV-irradiation at 254 nm for 1 h after thermal annealing. (a5, b5 and a6, b6) Cross section curves according to the thin film (direction follows the red arrows).
photoinduced molecular arrangement, when the quenching is reduced between the molecular layers.

4. CONCLUSION

In summary, a novel azo-functionalized liquid crystal material, APDPD, which is endowed with photochromic, thermal, and semiconductor characteristics altogether, was synthesized and corresponding OTFTs were fabricated. In the thermal annealing treatment process, highly ordered liquid crystal phase (SmX) with good orientation of the molecules facilitates better device performance. Compared with all the thermally treated devices, carrier mobilities of thin-film transistors achieved greatly improvement with the highest mobility of 0.875 cm² V⁻¹ s⁻¹ after UV-irradiation for 1 h, and it is mainly due to the synergistic effect of photoisomerization and photoinduced molecular arrangement. This type of multifunctional materials will provide reference for future researches to realize their potential applications in optoelectronic devices, such as optical sensors, memories, logic circuits, and functional switches.

■ ASSOCIATED CONTENT

* Supporting Information
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Notes
The authors declare no competing financial interest.

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Figure 6. (a) Ball-and-stick model of APDPD calculated by Multwfn (version 3.3.9). (b) X-ray diffraction patterns of APDPD thin film with different treatment methods: RT (black line), 100 °C annealing (red line), 150 °C annealing (blue line), 200 °C annealing (green line), and UV irradiation at 254 nm for 1 h of the thin films at RT (pink line).

Figure 7. STM constant-current images of APDPD molecules on Au(111). (a) 90 × 90 nm², (b) 18 × 18 nm², (c) 9 × 9 nm² (the measured unit cell parameters for this fishbone-shaped structure are a = 1.0 ± 0.1 nm, b = 4.2 ± 0.1 nm, and α = 94 ± 1°). (d) STM manipulation images of APDPD molecules on Au(111).

1H NMR spectrum and 13NMR spectrum, simplified graph of the sublimation, high-resolution mass spectrum, UV—vis spectra, differential scanning calorimetry analysis (DSC) for three cycles, polarizing optical microscope (POM) images of smectic A phase, the reversibility of photosensitive property of the device, diagrammatic sketch of the molecular packing structure, AFM images of APDPD thin films annealed at 150 °C and corresponding cross section curve (PDF)


