

WILEY-VCH

Toward Photo-Triggered Highly-Efficient Data Storage by Utilizing a Diketopyrrolopyrrole-Based Photoelectronic Small Molecule

Yang Li,^[a] Hua Li,^{*[a]} Jinghui He,^[a] Qingfeng Xu,^[a] Najun Li,^[a] Dongyun Chen,^[a] and Jianmei Lu^{*[a]}

Abstract: A photoelectrical cooperative strategy is proposed to effectively modulate the performance of multilevel data storage device. Through taking advantages of organic photoelectronic molecule as storage media, the fabricated device exhibits enhanced working parameters under the action of both optical and electrical input. In cooperation with the UV light, the operating voltages of the memory device are reduced, which is beneficial to the low energy consumption. Also, the ON/OFF current ratio becomes more tunable and facilitates the high-resolution multilevel storage. Compared with the previous methods of focusing on tuning the storage media, this study provides an easy approach to optimize organic device by exerting multiple physical channels. More importantly, it reveals an encouraging prospect for achieving multi-functionalities integrated high-density data storage devices.

Introduction

Over the past years, organic memory devices (OMDs) have aroused particular promises for realizing the new-generation of storage technology.^[1-5] OMDs could realize high-density data storage through multilevel memories, leading to an exceptional increase of storage capacity.^[6-10] Besides, the target of practical implement inspires extensive exploring efforts to optimize the working parameters of multilevel memory device. However, most strategies are focused on modulating the local structure of active layer, including tailoring molecular planarity,^[11] introducing different donor-acceptor (D-A) systems,^[10] single atom substitution,^[12] and molecular doping.^[13] These techniques are effective but also facing the challenges of complex synthetic work, finding suitable engineering method and uncontrollable experimental results.^[14,15] Moreover, these strategies are usually confined to a single electrical stimulus, which hinder the exploration of combining multiple physical channels (e.g., optical, electrical, and magnetic multi-input) into one electronic device.^[16,17] Currently, the integration of multi-functionalities into a microelectronic platform has been regarded as an alternative solution for the downscaling limits of the post-Moore information storage era.^[18] Nevertheless, it is still challenging to fulfill multifunctional integration within a single device for the sake of highly-efficient photoelectronic data-storage application.^[16]

In this contribution, we have achieved a novel multilevel

Supporting information for this article is given via a link at the end of the document.

memory device that can respond to optical and electrical cooperation. This memory device employed an organic diketopyrrolopyrrole (DPP)-containing photoelectronic molecule as the storage media, and exhibited prominent improvements of performance under photoelectrical co-stimulus. The DPP-based compounds are promising photoactive materials.^[19-21] There has been an intensive effort to construct DPP-based materials for photovoltaic applications, and the relevant solar cell devices with high power conversion efficiencies (PCEs) over 8% were reported by Heeger,^[22] Janssen,^[23] and Yang^[24] et al. Accordingly, the DPP-containing molecule possesses a potential photoactive property. This opens up the possibility of exploiting the photoelectronic cooperative effect into a single electrical switching memory device.

Herein, an A-D-A type DPP-based small molecule was synthesized to fabricate the organic multilevel memory prototype device. This molecule is symmetric (NI₂T₂DPP, Scheme 1) in which the DPP core and naphthylimide (NI) side-group serve as electron acceptors, and thiophene acts as electron donor. NI moiety was adopted due to its extra photosensitivity, $^{\left[25,26\right]}$ which enhances the potential photoelectronic property of NI₂T₂DPP. The photoelectrical cooperation effectively tunes the tristable switch behaviors of NI_2T_2DPP based memory device. Under modulated UV light, the device shows improved working parameters, in particular the lower threshold voltages. Since the energy consumption of electronic devices has become a significant issue,^[2,27] scaling down the threshold voltages is crucial for achieving low-cost multilevel memories. In addition, the current level of resistive state is enhanced, which makes enlarging the ON/OFF current ratio feasible. As expected, the fabricated device exhibits an optical responsive property, which enlightens future opportunities for operating memory switches by the self-generated photocurrent of photoactive storage media. We envision that utilizing the photoelectric properties of photoactive molecules could provide a very promising strategy to realize high-performance multilevel storage and further design new multifunctional devices.

Results and Discussion

Synthesis and Characterization

 NI_2T_2DPP was successfully synthesized from dithienyl-DPP precursor (1) according to Scheme 1 (detailed experimental procedures are given in the Supporting Information). Thermo gravimetric analysis (TGA) was carried out to examine the thermal stability of NI_2T_2DPP . The compound exhibited good thermal stability with decomposition temperature (5% weightloss) to be about 292 °C, which favors the device longevity (Supporting Information, Figure S1).

Y. Li, Prof. H. Li, Prof. J. He, Prof. Q. Xu, Prof. N. Li, Prof. D. Chen, Prof. J. Lu
College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Suzhou Nano Science and Technology
Soochow University
Suzhou 215123, P. R. China
E-mail: lihuaw@suda.edu.cn, lujm@suda.edu.cn

WILEY-VCH



Scheme 1. Synthesis of DPP-containing NI₂T₂DPP Molecule. Conditions: (i) 2-thiophenylboricacid, Pd₂(dba)₃, P(o-tol)₃, K₂CO₃, aliquat 336, toluene/distilled water, 90°C; (ii) NBS, CHCl₃, 0 °C then RT; (iii) 0.45 equiv of 3, Pd₂(dba)₃, P(o-tol)₃, K₂CO₃, aliquat 336, toluene/distilled water, 90°C.

Photoelectrical Memory Device Performance

The current–voltage (*I–V*) characteristics of the ITO/NI₂T₂DPP/AI sandwich memory device were measured as shown in Figure 1. Firstly, the three sweeps in Figure 1a were scanned in the dark environment. In the first sweep from 0 to -5.0 V, two changes in current occurred at the switching threshold voltages of -1.91 and -3.35 V, respectively. The device exhibited a ternary memory behavior, consisting of two electrical transitions from the low-conductance (OFF) state to an intermediate-

conductance (ON1) state, and finally to a high-conductance (ON2) state. In the subsequent negative scan from 0 to -5.0 V (sweep 2) and positive sweep from 0 to +5.0 V (sweep 3), the device remained at the high-conductance state. Even after removing the power supply or applying a reverse voltage, the device showed nonvolatile write-once read-many-times (WORM) memory characteristics.

In order to achieve the photoelectric cooperative effect, the device was further tested under UV light of 365 nm. The response time of UV light induction was determined to be about



Figure 1. (a) Current–voltage (I-V) characteristics of NI₂T₂DPP based memory device in the dark environment. (b) Current–voltage (I-V) characteristics of NI₂T₂DPP based memory device under UV light. The inset of (a,b) shows the schematic illustration of the sandwich memory device, composed of ITO substrate, organic layer and AI electrode. (c) The stability of memory device at a constant voltage stress (-1.0 V) in the dark. (d) The stability of memory device at a constant voltage stress (-1.0 V) in the dark. (d) The stability of memory device at a constant voltage stress (-1.0 V) under UV light.

15s (Supporting Information, Figure S2). Figure 1b shows a typical testing result. As can be seen, the features of the LV curves were similar to those measured in the dark (sweep 1-3). The device also maintained WORM memory behavior. However, the two threshold voltages were reduced to -1.32 and -2.88 V, which were lower than those in the dark (-1.91 and -3.35 V). The lower operating voltages are desirable for realizing low power-consuming multilevel memory devices.^[28] In addition, the current of the resistive state was increased, which opens the new potential of modulating ON/OFF current ratio. The suitable ON/OFF ratio is crucial for the memory device to implement high-resolution and low-error-rate data storage.^[29] Compared with the single electrical input, the simple combination of optical and electrical stimulus enhances the device performances. This finding is interesting since most previous studies about multilevel memories focused on improving the device performance through altering storage media, whereas few studies paid attentions to the multifunctional physical channels. These results suggest that the photoelectric cooperation is an effective strategy to modulate the working parameters of multilevel data-storage devices. Furthermore, it inspires the possibility of realizing memory switches through the self-generated photocurrent of photoactive storage media, which is now under way.

The stabilities of the device in the dark and under UV light were evaluated via retention time test under a constant stress of -1.0 V, respectively. As shown in Figure 1c and 1d, no obvious current degradation for each state was observed for at least 10^4 s. This manifests that the device is stable under voltage stress.

In addition, we studied the long-term device operation under UV light (Supporting Information, Figure S3). During the test, there is no obvious decay or degradation for the resistive memory switching behavior, which indicates that the device is stable to the long-term UV exposure. Moreover, I-V characteristics of the device show little change after 3 months even without the protection of encapsulation, which benefits for the practical longevity of multilevel storage memory (Supporting Information, Figure S4). We also investigated the repeatability of the memory behavior via a statistic on 100 device storage cells. Despite the loss of some cells, nearly 70% device cells exhibited the phototriggered improvement of memory performances, which implies a satisfactory reproducibility. We further counted the statistical distributions of switching current levels and threshold voltages of all the operative storage cells in the dark and under UV light (Supporting Information, Figure S5). In cooperation with the UV light, it can be noted that the mainly-centralized distributions of current levels become higher while those of threshold voltages show decreasing trends, which are consistent with the I-Vmeasurements (Figure 1a and 1b). These statistical results manifest that the photoelectrical cooperative effect could indeed enhance the multilevel memory performance of NI₂T₂DPP based device.

Molecular Electronic Properties and Memory Mechanism

To get insight into the mechanism of the tristable memory



Figure 2. (a) UV-vis absorption spectra of NI_2T_2DPP in THF solution and as a film on a quartz plate. (b) Cyclic voltammogram curve of NI_2T_2DPP in the thin film on ITO glass at a scan rate of 100 mV s⁻¹. (c) HOMO and LUMO energy levels diagram for NI_2T_2DPP along with the work function of the electrodes (ITO and Al). (d) DFT molecular simulation results of NI_2T_2DPP : molecular electrostatic potential (ESP), HOMO and LUMO molecular orbitals.

For internal use, please do not delete. Submitted_Manuscript

WILEY-VCH

WILEY-VCH

switching and the photoelectrical cooperative effect, we explored the molecular electronic properties of NI₂T₂DPP using optical and electrochemical measurements, as well as the density functional theory (DFT) simulations. The UV-visible absorption spectra of NI₂T₂DPP in solution and thin film are shown in Figure 2a. In solution state, NI₂T₂DPP shows a low-energy band from 500 to 700 nm, which can be attributed to the intramolecular charge transfer (ICT).^[30] In thin film, the absorption onset of NI_2T_2DPP presents a λ_{max} at 712 nm while the absorption onset is determined to be at 783 nm ($E_g = 1.58 \text{ eV}$). Compared with some other reported DPP-based small molecules, the optical band gap is relatively small, manifesting that the D-A intramolecular charge transfer and the intermolecular interaction of NI₂T₂DPP are strong enough to obtain high charge mobility.^[31] In addition, NI₂T₂DPP thin film displays a much broader absorption band and an apparent vibronic shoulder peak, which is likely due to the formation of molecular aggregation in the solid state.[32,33]

As shown in Figure 2b, cyclic voltammetry (CV) was adopted to estimate the electrochemical properties of NI₂T₂DPP. The CV curve exhibits onset reduction and oxidation peaks at -0.84. 0.67 and 1.32 V, which correspond to the LUMO, HOMO, and HOMO-1 energy levels of -3.52, -5.03 and -5.68 eV, using the equation $E_{\text{LUMO/HOMO}} = -e (4.8 - E_{\text{Ferrocene}} + E_{\text{red/oxd}}^{\text{onset}}) \text{ eV}.^{[23]}$ The electrochemical band gap is 1.51 eV for NI₂T₂DPP, which is comparable with the aforementioned optical property (1.58 eV). The detailed energy levels of molecular orbitals as well as the work function of electrodes are illustrated in Figure 2c. The hole injection energy barrier of NI2T2DPP (difference between ITO and HOMO) is estimated to be 0.23 eV, which is smaller than the electron injection energy barrier (0.78 eV, difference between AI and LUMO). This indicates that hole injection process is easier than electron injection. Therefore, the charge conduction process of ITO/NI2T2DPP/AI device is dominated by the hole injection.^[34] Moreover, it can be seen that the HOMO level closely approaches the work function of ITO electrode, which is favorable to the charge injection.^[35]

DFT calculations were further performed to simulate the HOMO and LUMO frontier molecular orbitals and electrostatic potential (ESP) of NI2T2DPP. Computation was executed with generalized gradient approximation (GGA) in DMol3 code, using unrestricted BLYP/DNP level. It can be seen that the HOMO and LUMO orbitals were unevenly distributed (Figure 2d). The electrons of HOMO mainly locate on the donors while the electrons of LUMO mainly distribute on the acceptors. These electron density distributions generally indicate that the ICT between donors and acceptors occurs upon the HOMO to LUMO transition.^[36] In addition, the calculated molecular surface shows continuous positive molecular ESP surface (in white and red) throughout the conjugated backbone (Figure 2d), which forms an open channel for charge carrier migration. However, negative ESP regions (in blue) arising from the DPP and NI acceptors also exist. These negative regions could function as "traps" to hinder the motion of charge carriers, leading to charge retention and memory effects.^[37] Under a low external bias, charge carriers could not get sufficient energy to surmount the injection barriers between the donors and acceptors. Thus, the device stays in low current, displaying a limited conductivity (OFF state). When the first threshold voltage reaches, charge carriers gradually obtain adequate activation energy and inject from the donors to acceptors. Therefore, the device displays increased conductivity and switches from OFF to ON1 state. However, the traps caused by different acceptors may not be filled simultaneously: the trap of DPP is completely filled whereas the trap of NI is partly unfilled.^{[11,38} This could be ascribed to the larger depth of NI trap, which corresponds to the stronger electron-withdrawing ability of NI than DPP.^[39] The depth values of two traps are simulated according to the reported literature (Supporting Information, Figure S6).^[40] The calculated molecular orbitals for DPP and NI imply that the depth of DPP trap is about 0.86 eV while that of NI is increased to 1.79 eV. The energy depth of NI is larger, which indicates that NI trap may demand more injection energy to be filled. As the second threshold voltage is approached, the accumulated charges with sufficient activation energy will fill the trap of NI, forming a "trapfree" environment with higher conductivity (ON2 state). Therefore, the device exhibits ternary memory characteristics, attributed to the two charge traps resulting from NI and DPP acceptors.^[40] Furthermore, the trapped charges could be stabilized by the intra- or intermolecular charge transfer process at the excited state, forming a charge-separated state.[41,42] These trapped charge carriers could not be easily released after removing the electric field or under reverse voltage bias. Consequently, the high-conductance state could be long-time maintained, indicative of nonvolatile WORM memory behavior.

Moreover, when the device is exposed to an UV light, external light could provide activation energy to excite the electrons at the HOMO orbital and promote the electron transfer. As a consequence, more holes are transported from the anode to the active layer (hole injection), resulting in an accumulation of charges carriers and a redistribution of the electrical field.^[17] The hole injection becomes more convenient and the accumulated charge carriers can more easily transport to the charge-trapping sites under the action of photoelectric synergistic effect. This suggests that the device could switch to the higher conductance state at lower threshold voltage. Also, the more photoinduced holes make it easier to migrate within the molecular backbone, which leads to better conductivity for each resistive state and thus causes higher current level. Accordingly, the photoelectric cooperative effect could effectively modulate the threshold voltages and ON/OFF current ratio, which provides an easy strategy to optimize the device performance instead of altering the organic active layer.

Film Surface Morphology and Internal Nanostructure

To further understand the long-term reliability of NI₂T₂DPP based memory device performance, we also investigated the surface morphology and internal microstructure of the organic layer, and the interfacial effects between the film and the electrode. As depicted in Figure 3a, atomic force microscopy (AFM) height images of the small-molecule thin film shows a maple-leaf-like structure with a regular surface roughness (root-mean-square roughness (R_{RMS}) = 2.72 nm, Figure 3b). The

WILEY-VCH

10.1002/asia.201600692



Figure 3. (a,b) AFM topographic image (a) and corresponding cross-section profile (b) of NI₂T₂DPP film spin-coated on ITO substrate, the scan size is 5 μ m×5 μ m. (c) XRD pattern obtained from NI₂T₂DPP spin-coated thin film. (d) Schematic geometry of the small-angle X-ray scattering under grazing incident angles (GISAXS) with a 2D image plate. The *z*-axis is normal to the substrate surface, the *x*-axis is along the surface parallel to the beam, and the *y*-axis is perpendicular to it. β and ϕ are the exit angles with respect to the film surface and to the incident plane respectively. (e) GISAXS pattern of NI₂T₂DPP spun on ITO-coated substrate. (f) Illustration of highly-oriented NI₂T₂DPP molecular grains with a preferred orientation along the substrate normal.

regular morphology can promote the charge-carrier transport between thin film and electrodes.^[43]

The X-ray diffraction (XRD) pattern was characterized to examine the internal molecular microstructure. As shown in Figure 3c, NI₂T₂DPP thin film clearly exhibits a primary diffraction peak with relatively high intensity at $2\theta = 6.6^{\circ}$, which suggests a high degree of crystallinity and molecular ordering.^[44] This diffraction can be attributed to the lamellar spacing peak, corresponding to a *d*-spacing of 13.38 Å.^[45] In addition, another small peak is observed at $2\theta = 27.0^{\circ}$, which can be assigned to the intermolecular π - π stacking peak with π - π stacking distance of ~3.30 Å. $^{[31]}$ The above XRD results indicate that a well-ordered lamellar packing structure is formed in NI2T2DPP thin film. Moreover, this π - π stacking distance is relatively small as compared with those of most other reported DPP-based conjugated molecules (usually 3.60-3.90 Å), [31,46,47] indicative of close intermolecular interaction among the donor/acceptor (D-A) conjugated backbone of NI₂T₂DPP.

Meanwhile, for the organic thin film, two-dimensional grazingincidence small-angle X-ray scattering (GISAXS) analysis is a powerful tool to determine the nanostructure of films relative to the substrate surface.^[48,49] As shown in Figure 3d, the sample (film on substrate) was impinged by the monochromatic X-ray beam with a very small glancing angle of 0.2°. GISAXS pattern of NI₂T₂DPP shows an elliptic peak along the q_z plane (q_{xy} = 0), suggesting that NI₂T₂DPP film is highly-oriented and crystallizes into a lamellar packing motif (Figure 3e).^[11] The scattering peak corresponds to a spacing distance of 13.62 Å, which is in good agreement with the observed XRD lamellar spacing data (13.38 Å). Moreover, this appearing signal along the q_z direction implies that the molecular grains of NI₂T₂DPP are of uniform orientation, with an out-of-plane configuration toward the ITO substrate surface (see illustration in Figure 3f).^[48] Such effective normal-tosubstrate alignment guarantees the connectivity between molecular grains, which reduces the defective or disordered contacting area of crystalline regions, and hence facilitates the formation of efficient transport pathways for charge carriers.^[50]

It has been reported that intermolecular interactions could play a significant role in controlling the thin film growth.^[44,51] In order to understand the highly-ordered film texture of NI₂T₂DPP, we take the intermolecular interaction into consideration. The XRD analysis reveals that there exist short-distance π - π stacking

interactions between NI₂T₂DPP molecules. Due to these shortdistance cofacial interactions, NI₂T₂DPP molecules are guided to grow in a similar face-to-face packing motif, thereby forming a well-ordered layer-by-layer structure. Therefore, there is energy benefit for NI₂T₂DPP to adopt the oriented molecular alignment. In organic electronics, the charge transport in two principal transport directions (in-plane and out-of-plane orientations) is usually focused, which dictates good relation with the device performance.^[49] As the memory device comprises vertically arranged electrodes (top AI and bottom ITO), the ordered molecular grains along the substrate normal can align with the direction of principal out-of-plane charge transport, and thus benefit the device operation. This correlation could account for the high reliability of memory device performance.

Conclusions

In summary, an organic DPP-containing photoelectronic molecule (NI₂T₂DPP) has been adopted as media of multilevel storage. This compound has a potential photoactive property and forms a well-organized lamellar structure in the solid state. Moreover, the NI₂T₂DPP based device can respond to the dual-stimulus of optical and electrical channels, displaying enhanced ternary memory behavior. Under the modulated UV light, the operating voltages of memory device are decreased, accompanied with the higher current level. These improved parameters are beneficial to the realization of low energy-consuming and high-resolution organic multilevel storage device. This work offers a promising photo-triggered strategy for improving memory device performance, and opens up potential prospect for designing multifunctional high-density data storage materials.

Experimental Section

Materials

2-Thiophenecarbonitrile, diisopropyl succinate, 2-ethylhexyl bromide, *N*bromosuccinimide, 2-thiophenylboricacid, 4-bromo-1,8-naphthalic anhydride, *n*-octylamine, bis(pinacolato)diboron, *N*,*N*-dimethylformamide (DMF) was distilled under argon atmosphere from calcium hydride (CaH₂) prior to use. Unless otherwise noted, all other solvents and reagents were of reagent grade and used as received without further purification.

Preparation of NI₂T₂DPP

2,5-Diethylhexyl-3,6-bis(5-bromothiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione (1) and 2-octyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (4) were synthesized following the previously published procedures.^[11,52] The detailed synthesis of the final product NI₂T₂DPP was given as below.

Synthesis of 6,6'-(5',5'''-(2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis([2,2'-bithiophene]-5',5-diyl))bis(2-octyl-1H-benzo[de]isoquinoline-1,3(2H)-dione) (Nl₂T₂DPP). Compound 3 (381 mg, 0.45 mmol), 4 (430.7 mg, 0.99 mmol), anhydrous

WILEY-VCH

potassium carbonate (585 mg, 4.24 mmol), toluene (8.5 mL) and distilled water (2.1 mL) were charged with a 50 mL Schlenk tube under argon protection. The mixture was degassed for 20 min before bis(dibenzylideneacetone)palladium (0) (Pd₂(dba)₃) (8.3 mg, 9.03 µmol), tri-o-tolylphosphine (P(o-tol)₃) (30.1 mg, 30.1 µmol) and 1 drop of aliquat 336 were added quickly. After subsequently degassed again for another 10 min, the reaction contents were heated at 90 °C for 24 h. The reaction mixture was cooled down to room temperature, extracted with dichloromethane and washed with distilled water and brine several times. The organic extract was dried over sodium sulfate and collected by rotary vacuum. Purification of the crude material through column chromatography on silica gel using a mixed mobile phase of dichloromethane and petroleum ether yielded NI₂T₂DPP as a dark-green solid (229 mg, 39%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.99 – 8.91 (m, 2H), 8.66 (d, J = 7.6 Hz, 4H), 8.61 (d, J = 7.5 Hz, 2H), 7.89 - 7.75 (m, 4H), 7.48 - 7.41 (m, 2H), 7.41 - 7.36 (m, 2H), 7.35 - 7.29 (m, 2H), 4.25 -4.16 (m, 4H), 4.14 - 3.98 (m, 4H), 2.00 - 1.89 (m, 2H), 1.79 - 1.69 (m, 4H), 1.43 - 1.25 (m, 36H), 0.96 - 0.84 (m, 18H). ¹³C NMR (151 MHz, CDCl₃, δ): 163.93, 163.64, 161.45, 141.70, 140.35, 139.34, 138.20, 137.78, 136.67, 131.69, 131.33, 130.48, 129.92, 129.44, 128.72, 128.59, 128.29, 127.30, 125.64, 125.18, 122.95, 122.14, 108.49, 45.92, 40.53, 40.26, 39.17, 31.72, 30.24, 29.25, 29.14, 28.43, 28.02, 27.07, 23.59, 23.03, 22.54, 14.02, 10.50; Anal. calcd for C78H86N4O6S4: C, 71.85; H, 6.65; N, 4.30; found: C, 71.57; H, 6.75; N, 4.43.

Memory Device Fabrication and Characterization

The NI₂T₂DPP based devices were fabricated on indium-tin-oxide (ITO)coated glass substrates. The ITO-coated glass substrates were precleaned with deionized (DI) water and ultrasonicated for 20 min each in DI water, acetone, and alcohol sequentially. The organic active layer of NI₂T₂DPP solution (10 mg/mL) was spin-coated onto each substrate at 300 RPM for 6 s, followed by 1500 RPM for 30 s. The film thickness of the active layer is about 90 nm (Supporting Information, Figure S7). Then the substrates were transferred into an evaporation chamber and pumped down to a vacuum of about 10⁻⁶ Torr. Finally, an aluminum layer with thickness of about 100 nm was thermal evaporated through a shadow mask onto the organic films. Current–voltage (*I–V*) measurements of the fabricated devices were performed without any encapsulation using a Keilthley 4200-SCS semiconductor system. A UV lamp with the wavelength of 365 nm was adopted as the UV illumination source during device characterization.

Measurement

All NMR spectra were acquired in chloroform-d with an Inova 400 MHz FT-NMR spectrometer unless otherwise noted. Data from elemental analysis were obtained by a Carlo-Erba EA-1110 instrument. Thermo gravimetric analysis (TGA) was conducted at a heating rate of 10 °C min⁻¹ with a TA instrument Dynamic TGA 2950 under a N₂ flow rate of 50 mL/min. UV-Vis absorption spectra were measured at room temperature with a Shimadzu UV-3600 spectrophotometer. Cyclic voltammograms were collected using a CorrTest CS Electrochemical Workstation analyzer with the assistances of an ITO working electrode, a reference electrode Ag/AgCl, and a counter electrode (Pt wire) at a sweep rate of 100 mV/s. Atomic force microscopy (AFM) measurements were performed to study the surface morphology of thin film with a MFP-3DTM (Digital Instruments/Asylum Research) AFM instrument, where topographical and phase images were acquired simultaneously. X-ray diffraction (XRD) patterns were obtained by an X'Pert-Pro MPD X-ray diffractometer. Grazing incidence small-angle X-ray scattering (GISAXS) measurements were conducted by an Anton Paar SAXS pace Analyzer. Scanning electron microscopy (SEM) image was performed using a Hitachi S-4700 scanning electron microscope.

The authors gratefully thank the NSF of China (21176164, 21206102, and 21336005), Chinese-Singapore Joint Project (2012DFG41900), the NSF of Jiangsu Province (BE2013052), and National Excellent Doctoral Dissertation funds (201455).

Keywords: multilevel storage • photoelectronic molecule • donor–acceptor system • photoelectrical cooperation • multifunctional integration

- [1] J. J. Yang, D. B. Strukov, D. R. Stewart, *Nat. nanotechnol.* 2013, *8*, 13.
- [2] W. P. Lin, S. J. Liu, T. Gong, Q. Zhao, W. Huang, Adv. Mater. 2014, 26, 570.
- [3] S. T. Han, Y. Zhou, V. A. Roy, Adv. Mater. 2013, 25, 5425.
- [4] J. C. Scott, L. D. Bozano, Adv. Mater. 2007, 19, 1452.
- [5] S. Song, B. Cho, T. W. Kim, Y. Ji, M. Jo, G. Wang, M. Choe, Y. H. Kahng, H. Hwang, T. Lee, *Adv. Mater.* **2010**, *22*, 5048.
- [6] C. T. Poon, D. Wu, W. H. Lam, V. W. Yam, Angew. Chem. Int. Ed. 2015, 54, 10569.
- [7] B. Hu, C. Wang, J. Wang, J. Gao, K. Wang, J. Wu, G. Zhang, W. Cheng, B. Venkateswarlu, M. Wang, P. S. Lee, Q. Zhang, *Chem. Sci.* 2014, 5, 3404.
- [8] C. Wang, P. Gu, B. Hu, Q. Zhang, J. Mater. Chem. C 2015, 3, 10055.
- [9] H. Wang, F. Meng, Y. Cai, L. Zheng, Y. Li, Y. Liu, Y. Jiang, X. Wang, X. Chen, Adv. Mater. 2013, 25, 5498.
- [10] H. Li, Q. Xu, N. Li, R. Sun, J. Ge, J. Lu, H. Gu, F. Yan, J. Am. Chem. Soc. 2010, 132, 5542.
- [11] Y. Li, H. Li, H. Chen, Y. Wan, N. Li, Q. Xu, J. He, D. Chen, L. Wang, J. Lu, Adv. Funct. Mater. 2015, 25, 4246.
- [12] Z. Liu, J. He, H. Zhuang, H. Li, N. Li, D. Chen, Q. Xu, J. Lu, K. Zhang, L. Wang, *J. Mater. Chem. C* 2015, 3, 9145.
- [13] B. Hu, X. Zhu, X. Chen, L. Pan, S. Peng, Y. Wu, J. Shang, G. Liu, Q. Yan, R. W. Li, *J. Am. Chem. Soc.* 2012, *134*, 17408.
- [14] C. Simão, M. Mas-Torrent, J. Casado-Montenegro, F. Otón, J. Veciana, C. Rovira, J. Am. Chem. Soc. 2011, 133, 13256.
- [15] T. Lee, S. U. Kim, J. Min, J. W. Choi, Adv. Mater. 2010, 22, 510.
- [16] H. Tan, G. Liu, X. Zhu, H. Yang, B. Chen, X. Chen, J. Shang, W. D. Lu, Y. Wu, R. W. Li, Adv. Mater. 2015, 27, 2797.
- [17] C. Ye, Q. Peng, M. Li, J. Luo, Z. Tang, J. Pei, J. Chen, Z. Shuai, L. Jiang, Y. Song, J. Am. Chem. Soc. 2012, 134, 20053.
- [18] L. Liu, R. Kumar, K. Huybrechts, T. Spuesens, G. Roelkens, E. J. Geluk, T. de Vries, P. Regreny, D. Van Thourhout, R. Baets, G. Morthier, *Nat. Photon.* 2010, *4*, 182.
- [19] K. H. Hendriks, W. Li, M. M. Wienk, R. A. Janssen, J. Am. Chem. Soc. 2014, 136, 12130.
- [20] C. M. Proctor, J. A. Love, T. Q. Nguyen, Adv. Mater. 2014, 26, 5957.
- [21] Y. Lin, L. Ma, Y. Li, Y. Liu, D. Zhu, X. Zhan, Adv. Energy Mater. 2013, 3, 1166.
- [22] H. Choi, S. J. Ko, T. Kim, P. O. Morin, B. Walker, B. H. Lee, M. Leclerc, J. Y. Kim, A. J. Heeger, *Adv. Mater.* **2015**, *27*, 3318.
- [23] W. Li, W. S. Roelofs, M. Turbiez, M. M. Wienk, R. A. Janssen, Adv. Mater. 2014, 26, 3304.
- [24] L. Dou, J. You, J. Yang, C.-C. Chen, Y. He, S. Murase, T. Moriarty, K. Emery, G. Li, Y. Yang, *Nat. Photon.* **2012**, *6*, 180.

- [25] J. Du, M. Hu, J. Fan, X. Peng, Chem. Soc. Rev. 2012, 41, 4511.
- [26] D. Kolosov, V. Adamovich, P. Djurovich, M. E. Thompson, C. Adachi, J. Am. Chem. Soc. 2002, 124, 9945.
- [27] X. Wang, W. Xie, J. B. Xu, Adv. Mater. 2014, 26, 5496.
- [28] S. G. Hahm, S. Choi, S. H. Hong, T. J. Lee, S. Park, D. M. Kim, W. S. Kwon, K. Kim, O. Kim, M. Ree, *Adv. Funct. Mater.* **2008**, *18*, 3276.
- [29] Y. C. Lai, F. C. Hsu, J. Y. Chen, J. H. He, T. C. Chang, Y. P. Hsieh, T. Y. Lin, Y. J. Yang, Y. F. Chen, *Adv. Mater.* **2013**, *25*, 2733.
- [30] T. L. Nelson, T. M. Young, J. Liu, S. P. Mishra, J. A. Belot, C. L. Balliet, A. E. Javier, T. Kowalewski, R. D. McCullough, *Adv. Mater.* **2010**, *22*, 4617.
- [31] Z. Yi, L. Ma, B. Chen, D. Chen, X. Chen, J. Qin, X. Zhan, Y. Liu, W. J. Ong, J. Li, *Chem. Mater.* **2013**, *25*, 4290.
- [32] J. Liu, Y. Sun, P. Moonsin, M. Kuik, C. M. Proctor, J. Lin, B. B. Hsu, V. Promarak, A. J. Heeger, T. Q. Nguyen, *Adv. Mater.* **2013**, *25*, 5898.
- [33] J. Wang, K. Shi, Y. Suo, Y. Lin, G. Yu, X. Zhan, J. Mater. Chem. C 2016, 4, 3781.
- [34] S. Park, K. Kim, D. M. Kim, W. Kwon, J. Choi, M. Ree, ACS Appl. Mater. Interfaces 2011, 3, 765.
- [35] X. Guo, R. P. Ortiz, Y. Zheng, Y. Hu, Y. Y. Noh, K. J. Baeg, A. Facchetti, T. J. Marks, J. Am. Chem. Soc. 2011, 133, 1405.
- [36] W. Y. Lee, T. Kurosawa, S. T. Lin, T. Higashihara, M. Ueda, W. C. Chen, *Chem. Mater.* 2011, 23, 4487.
- [37] Q. D. Ling, D. J. Liaw, C. Zhu, D. S. H. Chan, E. T. Kang, K. G. Neoh, *Prog. Polym. Sci.* 2008, 33, 917.
- [38] Y. Li, H. Li, J. He, Q. Xu, N. Li, D. Chen, J. Lu, Chem. Asian J. 2016, 11, 906.
- [39] P. Y. Gu, F. Zhou, J. Gao, G. Li, C. Wang, Q. F. Xu, Q. Zhang, J. M. Lu, J. Am. Chem. Soc. 2013, 135, 14086.
- [40] Q. D. Ling, Y. Song, S. L. Lim, E. Y. Teo, Y. P. Tan, C. Zhu, D. S. Chan, D. L. Kwong, E. T. Kang, K. G. Neoh, *Angew. Chem. Int. Ed.* **2006**, *45*, 2947.
- [41] A. D. Yu, T. Kurosawa, Y. H. Chou, K. Aoyagi, Y. Shoji, T. Higashihara, M. Ueda, C. L. Liu, W. C. Chen, ACS Appl. Mater. Interfaces 2013, 5, 4921.
- [42] H. J. Yen, H. Tsai, C. Y. Kuo, W. Nie, A. D. Mohite, G. Gupta, J. Wang, J. H. Wu, G. S. Liou, H. L. Wang, *J. Mater. Chem. C* 2014, 2, 4374.
- [43] S. L. Lian, C. L. Liu, W. C. Chen, ACS Appl. Mater. Interfaces 2011, 3, 4504.
- [44] J. S. Ha, K. H. Kim, D. H. Choi, J. Am. Chem. Soc. 2011, 133, 10364.
- [45] H. J. Yun, G. B. Lee, D. S. Chung, Y. H. Kim, S. K. Kwon, Adv. Mater. 2014, 26, 6612.
- [46] M. S. Chen, O. P. Lee, J. R. Niskala, A. T. Yiu, C. J. Tassone, K. Schmidt, P. M. Beaujuge, S. S. Onishi, M. F. Toney, A. Zettl, J. M. Frechet, J. Am. Chem. Soc. 2013, 135, 19229.
- [47] Y. Li, P. Sonar, S. P. Singh, M. S. Soh, M. van Meurs, J. Tan, J. Am. Chem. Soc. 2011, 133, 2198.
- [48] Q. Zhang, J. He, H. Zhuang, H. Li, N. Li, Q. Xu, D. Chen, J. Lu, Adv. Funct. Mater. 2016, 26, 146.
- [49] J. Rivnay, S. C. Mannsfeld, C. E. Miller, A. Salleo, M. F. Toney, *Chem. Rev.* 2012, 112, 5488.
- [50] E. Verploegen, R. Mondal, C. J. Bettinger, S. Sok, M. F. Toney, Z. Bao, *Adv. Funct. Mater.* **2010**, *20*, 3519.
- [51] M. S. Chen, J. R. Niskala, D. A. Unruh, C. K. Chu, O. P. Lee, J. M. J. Fréchet, *Chem. Mater.* 2013, 25, 4088.
- [52] L. Dou, J. Gao, E. Richard, J. You, C. C. Chen, K. C. Cha, Y. He, G. Li, Y. Yang, J. Am. Chem. Soc. 2012, 134, 10071.

FULL PAPER

A photoelectrical cooperative strategy is proposed to effectively improve the working parameters of ternary memory storage device. By taking advantages of organic photoelectronic molecule as storage media, this study opens up the possibility of integrating multi-functionalities into a single device for highly-efficient multilevel data storage.



Yang Li, Hua Li, Jinghui He,* Qingfeng Xu, Najun Li, Dongyun Chen, and Jianmei Lu*

Page No. – Page No.

Toward Photo-Triggered Highly-Efficient Data Storage by Utilizing a Diketopyrrolopyrrole-Based Photoelectronic Small Molecule

WILEY-VCH