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Controlled deposition of large-area and highly-ordered thin films: effect of dip-coating-induced morphological evolution on resistive memory performance<sup>†</sup>

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Developing a simple, versatile and efficient technique that satisfies both large-scale production and nano-scale control is highly desirable but very challenging for achieving high-performance organic-based memory electronics. Herein, we employed a dip-coating method to fabricate reliable and cost-effective organic memory devices (OMDs). This technique can allow us to deposit high-quality, homogeneous and large-area nanopatterns on the surfaces of thin films and realize uniform OMD performances with a record reproducibility up to 96%. To the best of our knowledge, this is the first report about dip-coated OMDs with the highest reproducibility observed to date, which demonstrates the promising versatility of dip-coating technique to fabricate organic memories and its suitability to scale-up for high-throughput solution processing.

#### Introduction

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Organic memory devices (OMDs) have become a research focus for a long time owing to their outstanding merits such as low cost, light weight, high information-storage capacity and possibility to mimic biological synapses.1-14 In particular, attributing to the rapid development of solution-processing techniques, a variety of solution-processable materials have come to the forefront,<sup>15-19</sup> which remarkably accelerate the far-behind exploiting process of organic electronics. Recently, most of the solution-processed OMDs are fabricated from spin-coating or drop-casting methods,<sup>20-25</sup> which have been proved useful for small-scale film deposition. However, such solution-coating processes usually suffer from a drawback that restricts their range of application and makes scaling them up difficult: Clearly, it is challenging to develop a general principle for the preparation of uniform and continuous thin films over large areas. Besides, these techniques often produce inhomogeneous patches or films that contain lots of disordered grains and grain boundaries,<sup>26,27</sup> which could severely impede their charge transport properties. Therefore,

it is of high importance to develop a simple but efficient solution-processed method for OMDs fabrication, which combines both large-scale production and small-scale deposition control.

Currently, some researchers have put forward the strategy of thermal or solvent annealing as a post-processing step for promoting the solution-coated film morphologies.<sup>28-31</sup> For instance, due to the controlled nucleation and crystallization of film grains via solvent annealing, Loo et al. demonstrated that the device mobility of soluble acene-based organic thin-film transistors (OTFTs) was two orders of magnitude increased.<sup>32</sup> Nevertheless, thermal or solvent annealing could hardly guarantee uniformity over the entire film surface, which often causes energy waste and complicates the device fabrication processes.<sup>33</sup> To address the aforementioned issues, herein, we report a novel technique for OMDs fabrication that is precisely controlled by a facile, straightforward and versatile dip-coating method. Dip-coating can strategically induce the film growth using a suitable set of programmed parameters. This technique can not only facilitate the self-assembly of wellpatterned films in nano-scale control,<sup>34,35</sup> but also enable to achieve large-area coverage,36,37 which benefits to integrate devices into large scale. In addition, dip-coating does not produce too much viscous stresses on organic molecules comparing to current approaches (e.g., spin-coating),<sup>38</sup> thereby effectively inhibiting the crack formation, shrinkage, and irregular edge effects. Although dip-coating holds these attractive advantages, it is very surprising that such method has less been utilized to fabricate OMDs. To our best knowledge, this study is the first demonstration of OMDs via dip-coating with a record reproducibility, which provides a simple and reliable solution-processing technique to realize a

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<sup>†</sup> Electronic Supplementary Information (ESI) available: Experimental details, thermal properties, AFM images of the spin-coated thin films, statistical reproducibility and SET voltage distributions, the retention stabilities of dip-coated OMDs, and X-ray crystallographic information file (CCDC 1870372). See DOI: 10.1039/x0xx00000x

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**Fig. 1** (a–c) Molecular geometries of (a) **NIBe**, (b) **NIQu** and (c) **NIPy** with the increasing molecular conjugation. (d) Schematic presentation for the preparation of large-area, highly-ordered and uniform molecular films by an optimized dip-coating process.

controlled uniformity over large areas (>  $\rm cm^2)$  and batch-to-batch OMD stability.

The analogues of 2-octyl-6-(5,6,7,8-tetraphenylnaphthalen-2-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (**NIBe**), 6-(9,14diphenylbenzo[*f*]tetraphen-11-yl)-2-octyl-1*H*-

benzo[*de*]isoquinoline-1,3(2*H*)-dione (**NIQu**) and 6-(9,14diphenyldibenzo[*de*,*qr*]tetracen-11-yl)-2-octyl-1*H*-

benzo[de]isoquinoline-1,3(2H)-dione (NIPy) (Fig. 1a-c) were employed here as prototypes for demonstrating the dipcoated OMDs. The selection of these series of molecules relies on the following considerations: (1) the intrinsic  $\pi$ - $\pi$ interaction between the aromatic planes and van der Waals interaction between the alkyl chains can cooperate to tackle the self-assembled nanostructures; (2) the increasing aromatic plane of these molecules holds the promise to achieve excellent charge mobility; and (3) the co-existence of phenyl and alkyl chains guarantees the solution-processed ability. Fig. 1d presents a schematic diagram of the simple and efficient fabrication process. The versatility of this method is demonstrated by systematic atomic force microscopy (AFM) inspection and more importantly, the ultimate OMDs performance. In our study, devices fabricated from the dipcoating technique showed far superior output performances as compared to those based on the spin-coating method. The stability and reproducibility of OMDs were nearly five-fold increased (up to a record value of 96% obtained to date) owing to the dip-coating-induced morphological evolution. This work highlights a versatile technique and general guideline to achieve nano-scale control over large areas, which would be

scalable for mass production of high-performance OMDs by a solution manufacturing process.

#### **Results and discussion**

#### Synthesis and Characterization of As-Prepared Molecules

**NIBe, NIQu** and **NIPy** were successfully synthesized by combining acene units and naphthalimide (NI) species together through palladium-catalyzed Suzuki–Miyaura cross-coupling reactions (Scheme S1†). The detailed synthetic procedures are provided in the ESI†. These as-prepared three molecules adopt the similar NI end-capped structure, and the only difference is the increased conjugation at the acene part. These three target products were confirmed by <sup>1</sup>H NMR (Fig. S1-S3†), <sup>13</sup>C NMR (Fig. S4-S6†), and elemental analysis. By introducing alkyl chains, **NIBe**, **NIQu** and **NIPy** show satisfactory solubility in the most common organic solvents such as chloroform, toluene, and dichlorobenzene. In addition, these three compounds exhibit good thermal stability, with an onset decomposition (5% weight-loss) temperature over 200 °C (Fig. S7†), respectively.

Moreover, the yellow plate-like crystals of **NIPy** were obtained by slow evaporation of mixed solvents (chloroform/isopropanol = 2:1) under ambient conditions, which further demonstrate the structure of this series of molecules. The single-crystal X-ray diffraction analysis reveals that the as-prepared crystal of **NIPy** belongs to a triclinic system with the following unit cell parameters: a = 9.7201(4), b

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**Fig. 2** Single-crystal X-ray structure of **NIPy**: (a) Molecular structure (H atoms are omitted for clarity) shows that two adjacent molecules form a dimer, where each acene part is marked with different colors. (b) The arrangement of the neighboring dimers shows a dense overlap on the NI groups (highlight by blue color). (c) The crystal packing mode corresponds to a layer-by-layer manner, separated by the acenes interdigitation. The mean central distance between the two  $\pi$ -overlapped NI planes is 3.53 Å. (d) The side view of the crystal packing mode.

= 20.7651(7), c = 22.6267(8) Å, and the Z value is 2 (Table S1†). Fig. 2a shows that one molecule is strongly affected by its adjacent molecule, where two adjacent molecules form a "dimer" structure. The neighboring dimers self-assemble into a layer-by-layer manner, which shows a dense overlap on the NI part (Fig. 2b), separated by the interdigitation of acenes. The mean central distance between the two nearest NI groups is 3.53 Å (Fig. 2c and 2d), which manifests that there are considerable interactions among the  $\pi$ -planes of neighboring **NIPy** molecules.<sup>39</sup>

#### **Optimization of the Dip-Coating Process**

To fabricate solution-processed devices, we firstly examined the solution-deposited behavior of these three compounds by spin-coating method. As shown in Fig. S8<sup>†</sup>, all AFM images of **NIBe**, **NIQu** and **NIPy** based spin-coated films exhibit unevenly aggregated domains, which are undesirable for highperformance device fabrication. Thus, a convenient, simple but efficient film-forming technique for morphological evolution is highly desirable. To this regard, the cost-effective dip-coating method successfully arouses our attention. Dip-coating allows precise nanostructural control over large areas, which offers the versatility for a large variety of organic materials.<sup>40</sup> On the other hand, **NIPy** possesses the highest conjugated plane, which could induce large molecular rigidity and thus decrease the soluble propensity, leading to a lower solubility comparing to **NIBe** and **NIQu**. For the solution-processed organic electronics, the molecular growth in thin films is highly dependent on the molecular solubility.<sup>41,42</sup> From this standpoint, we decided to optimize the dip-coating conditions for all three molecules through preferential systematic investigation of **NIPy**.

#### Solvent Selection

The appropriate selection of solvents usually plays a significant role in governing the molecular self-assembly behavior in thin films.<sup>38,43</sup> During the dip-coating process, molecular growth greatly relies on the synergistic effects of solute-exchange and solvent-evaporation rates. To determine the suitable dipcoating solvent for prototype NIPy, we chose three typical kinds of solvents (i.e., chloroform (CF), toluene (TL) and odichlorobenzene (ODCB)) that possess apparently different volatilities and investigated their corresponding film-forming properties. As shown in Fig. 3a, the film fabricated from CF shows quite disordered and unevenly aggregated domains with root-mean-square roughness (R<sub>RMS</sub>) of 2.95 nm. Most of these domains are larger than 1 um, which are undesirable for good device performance since they can largely impede charge injection. The film morphology from TL somewhat improves, however, still suffers from the irregular surface structure (RRMS

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Fig. 3 AFM height images of NIPy dip-coated films from different solvents of (a) CF, (b) TL and (c) ODCB onto indium-tin-oxide (ITO) substrates.



Fig. 4 AFM height images of NIPy dip-coated films from different concentrations of (a) 5 mg/mL, (b) 10 mg/mL and (c) 50 mg/mL solutions in ODCB.

= 2.48 nm, Fig. 3b). When dip-coating from ODCB is employed, **NIPy** film becomes much more uniform with smaller roughness of 0.80 nm (Fig. 3c), forming a high-quality and well-defined "granular" structure. The connectivity between neighboring crystalline grains is developed, which enables the efficient charge carriers transport. Such morphological improvement can be attributed to the low solvent-evaporation rate of ODCB, which allows for sufficient solute exchange and arrangement. Therefore, ODCB is a satisfactory solvent for dip-coated film fabrication.

#### **Solution Concentration Adjustment**

The concentration of molecular solution is another parameter that has a great impact on the film-forming behavior during dip-coating process.<sup>27,44</sup> The reliable concentration for dip-coating is closely correlated to the molecular structure, solubility and self-assembly property. Generally, the grain sizes

and film thickness at high concentration are larger than those at low concentration. In order to determine the appropriate molecular concentration for processing, we prepared 5 mg/mL, 10 mg/mL and 50 mg/mL solutions of NIPy in ODCB, which represent low, moderate and high concentration, respectively. The AFM image of film at low concentration (5 mg/mL) shows a continuous surface, but the film thickness is insufficient and the morphology is relatively amorphous with some domains  $(R_{RMS} = 1.26 \text{ nm}, \text{ Fig. 4a})$ . At the moderate concentration of 10 mg/mL, the film exhibits a bark-like structure and the thickness is enhanced. The uniformity of the film surface is guaranteed over a large area with regular roughness of 0.86 nm (Fig. 4b). However, when dip-coating from higher concentration of 50 mg/mL is conducted, the visible out-of-order crystalline islands (larger than 1 µm) emerge and suppress the homogenous surface ( $R_{RMS}$  = 2.44 nm, Fig. 4c). Thus, the concentration of 10mg/mL in ODCB is preferred as suitable processing condition for molecular dip-coating.

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Fig. 5 AFM height images of NIPy dip-coated films at different rates of (a) 10  $\mu$ m/s, (b) 40  $\mu$ m/s and (c) 160  $\mu$ m/s.



Fig. 6 AFM height images of (a) NIBe, (b) NIQu and (c) NIPy dip-coated films under the optimized conditions.

#### **Pull-Out Speed Investigation**

Generally, dip-coating is a powerful evaporation-controlled process and allows to establish a fine control of the evaporation rate through programming the pull-out speed of substrate, which can largely influence the film microstructures.<sup>36,45</sup> The morphological evolution as a function of withdrawal speed is related to the dynamical processes occurring at the three-phase solution/substrate/air contact line. By controlling the withdrawal speed, we are able to obtain a high-quality and uniform thin film quantitatively. To investigate the suitable pull-out speed, the pulling rate of substrate from the solution reservoir was gradually changed in three ranges: low, middle and high. Each substrate was dipped into the 10 mg/mL NIPy solution in ODCB and pulled out at a different rate of 10  $\mu$ m/s (low), 40  $\mu$ m/s (intermediate), and 160  $\mu$ m/s (high), respectively. As shown in Fig. 5a, at low speed of 10 µm/s, the film shows a homogeneous tiny-bark-like structure with a regular  $R_{\rm RMS}$  of 0.86 nm. As the pulling speed

increases to 40 µm/s, the aggregated crystalline domains appear, and the film surface becomes coarse with uneven grains ( $R_{\rm RMS}$  = 1.02 nm, Fig. 5b). Furthermore, when a higher speed of 160  $\mu\text{m/s}$  is utilized, the large-area arbitrarily shaped crystalline islands form among the film surface, which could severely impede the charge transport efficiency ( $R_{RMS} = 1.88$ nm, Fig. 5c). While pulling the substrate out of the solution at a high speed, there is no enough time for the sufficient soluteexchange and solvent-evaporation at the air/solution/substrate contact line. Thus, the film growth is mainly controlled by the subsequent evaporation of the solution that adheres to the substrate at atmosphere,<sup>46</sup> which resembles the drop-casting process and suffers from the discontinuous and uneven grains. Therefore, the withdrawal speed of 10  $\mu$ m/s is preferred, which warrants the adequate solute concentration gradient and hence affords the driving force for favorable film growth.

High-Quality Dip-Coated Thin Films of NIBe, NIQu and NIPy

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**Fig. 7** (a-c) Optical absorption spectra of (a) **NIBe**, (b) **NIQu** and (c) **NIPy** in ODCB solutions and dip-coated films on the ITO substrates. (d-f) Cyclic voltammogram curves of (d) **NIBe**, (e) **NIQu** and (f) **NIPy** at a scan rate of 50 mV s<sup>-1</sup>; the ferrocene/ferrocenium redox couple is used as an internal standard (-4.80 eV, the onset potential is 0.42 eV).

According to the optimized dip-coating conditions, the highlyordered films of NIBe, NIQu and NIPy were finally fabricated. The substrates were smoothly dipped into the 10 mg/mL ODCB solutions of NIBe, NIQu and NIPy, and pulled out at a constant rate of 10 µm/s, respectively. The high-quality and uniform nanostructural patterns are formed over large areas, as proven by AFM images. In comparison with spin-coated films, the selfassembly behaviors of dip-coated thin films are significantly enhanced (Fig. 6a-c). All films of the three molecules present the appearance of "bark-shape" morphologies. As the molecular conjugation increases, the grain sizes of the films become smaller and more homogenous throughout the surface. The film roughness decreases from 3.06 nm of NIBe to 1.75 nm of NIQu, and 0.86 nm of NIPy, which clearly indicates the increasing uniformity and flatness. More interestingly, for NIPy, some nanofibers (about 100 nm in width) are developed between the crystalline grains, which are conducive to the crystalline connectivity and thus facilitates the efficient charge transport.<sup>31</sup> Whereas the spin-coated films are prone to irregular patterns, dip-coating permits a high degree of morphological control, which offers particular advantages to implement large-area uniformity.

#### **Photophysical and Electronic Properties**

The optical properties of **NIBe**, **NIQu** and **NIPy** in ODCB solutions and dip-coated films were subsequently studied. Fig. 7a-c shows the normalized optical absorption spectra of these

three molecules. In solutions, all three compounds exhibit absorption bands between 220 and 450 nm. In dip-coated thin films, these series of molecules show two well-resolved absorption peaks located at ~340 and 450 nm, respectively. The high-energy absorption band at 340 nm arises from the molecular aromatic conjugation while the low-energy absorption band around 450 nm corresponds to the intramolecular charge transfer (ICT) process.<sup>47</sup> Compared with solution state, the onset absorption ( $\lambda_{onset}$ ) peaks of **NIBe**, **NIQu** and **NIPy** in films display obvious bathochromic shifts, which can be ascribed to the molecular self-assembly via dipcoating. The  $\lambda_{onset}$  of **NIBe**, **NIQu** and **NIPy** are 553, 549 and 547 nm, thus, their corresponding optical band gaps ( $E_g^{opt}$ ) are calculated to be 2.24, 2.26 and 2.27 eV ( $E_g^{opt} = 1240/\lambda_{onset}$ ).

Cyclic voltammetry (CV) was utilized to examine the electrochemical properties of **NIBe**, **NIQu** and **NIPy**. As shown in Fig. 7d-f, all three compounds can exhibit oxidation and reduction waves. The onset oxidation potentials of **NIBe**, **NIQu** and **NIPy** are 1.08, 1.34 and 1.33 V in the positive potential region, while the onset reduction potentials are -0.87, -0.94 and -0.90 V in the negative potential region, respectively. According to the equations  $E_{HOMO/LUMO} = -e$  ( $4.80 - E_{Fc} + E_{ox/red}^{onset}$ ) V, the highest occupied molecular orbital (HOMO) energies of **NIBe**, **NIQu** and **NIPy** are determined to be -5.46, -5.72 and -5.71 eV, respectively, whilst the lowest unoccupied molecular orbital (LUMO) energies are determined to be -3.51, -3.44 and -3.48 eV. Therefore, the electrochemical band gaps of **NIBe**, **NIQu** and **NIPy** are estimated to be 1.95, 2.28

and 2.23 eV, which are similar to the aforementioned optical band gaps. Moreover, the hole injection energy barriers of ITO/HOMO are calculated to be 0.66, 0.92 and 0.91 eV, while the electron injection energy barriers of aluminum (Al)/LUMO are calculated to be 0.79, 0.86 and 0.82 eV. For **NIBe**, the hole injection barrier is smaller than electron injection barrier, which indicates that hole injection dominates the charge conduction process.<sup>5</sup> However, as the molecular conjugation increases, the electron injection barrier becomes smaller than hole injection barrier, which suggests the potential of **NIQu** and **NIPy** as ambipolar or n-type semiconducting materials.<sup>48</sup> The extended aromatic conjugation benefits for the efficient electron delocalization, which is conducive to the electron transport.

#### **Resistive Memory Device Performance**

To inspect the electrical performances of **NIBe**, **NIQu** and **NIPy**, we deposited AI metal onto their optimal dip-coated films and fabricated the sandwiched OMDs as shown in Fig. 8a. The current–voltage (*I–V*) measurement illustrates that the **NIBe**-based device shows a FLASH-type binary memory behavior (Fig. 8b). When applying the negative voltage from 0 to -5.0 V, an abrupt increase in the current appears at -2.05 V (sweep 1), indicating that the device switches from a low-conductance state (LCS) to a high-conductance state (HCS). This LCS-to-HCS transition can act as a "writing" process in digital storage. The device remains its HCS during the next negative voltage pulse (sweep 2) and even after the removal of the electric field, which denotes the nonvolatile memory (NVM) nature. In

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addition, the HCS can be programmed to the veriginal LCS through a reverse positive scan (sweep 3, 1 WA (A 3 4 3 4 regarded as a digital "erasing" process. The recovered LCS can be stably read during the subsequent positive sweep (sweep 4) and successfully reprogrammed to HCS (sweep 5) in the next voltage scan. This "write-read-erase-read-rewrite" cycle corresponds to the binary FLASH memory behavior.<sup>14,20</sup>

Fig. 8c manifests the I-V characteristics of NIQu-based device. which shows similar а The "write-read-erase-read-rewrite" cycle. I-V curve demonstrates that **NIQu** also exhibits FLASH-type binary memory performance. However, the electrical measurement of NIPy-based device displays different resistive memory behavior. When switching from LCS to HCS, the HCS can be retained and could not be erased after removing the electric field or under reverse voltage pulse (Fig. 8d, sweep 1-3). This electrical switching phenomenon corresponds to WORM (i.e., write-once-read-many-times) type memory behavior. In addition, the more repeatable I-V sweeps denote the reliable memory performance of these devices (Fig. S9<sup>†</sup>). The LCS and HCS are well-separated with the current ratio of ~10<sup>3</sup>, which benefits for running their OMDs accurately.

Moreover, we investigated the fifty independent units of each kind of devices to verify their distinct memory types. As shown in Fig. S10<sup>†</sup>, the statistic result reveals that for **NIBe**, the proportion of FLASH-type memory remains around 74%. While for **NIQu**, the FLASH-type ratio markedly decreases (~50%) and several storage cells start to exhibit unrecoverable NVM behavior. As it comes to **NIPy**, most of the device cells



**Fig. 8** (a) Scheme of the OMDs architecture (composed of ITO, organic dip-coated films and Al electrode), which is connected with the *I–V* detector. (b-d) The detected *I–V* signals of (b) **NIBe**, (c) **NIQu** and (d) **NIPy** based memory devices; the numbers represent the sweeping sequences whilst the insets denote the optimized large-area dip-coated films.

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Molecule	NIBe	NIQu	NIPy
Molecular Conformation	55.1°	54.4°	53.9°
ESP			
LUMO			
номо	A CONTRACTOR OF STATE		
Electron Affinity	2.97 eV	3.02 eV	3.05 eV
HOMO-LUMO Band gap	2.16 eV	1.89 eV	1.83 eV

**Fig. 9** DFT calculated molecular conformation, ESP, HOMO and LUMO charge-density surfaces, electron affinities, and HOMO–LUMO band gaps of **NIBe**, **NIQu** and **NIPy** by the generalized gradient approximation (GGA) with unrestricted BLYP/DNP level.

(up to 96%) show non-erasable memory switching, which transform from FLASH-type into WORM-type performance. Notably, different from the spin-coating-based devices, which show quite unstable and non-identifiable output performances, the dip-coating-based devices hold highly-raised batch-to-batch reproducibility with a record uppermost value of 96% reported so far, which strongly demonstrates the adaption of dip-coating to highly-reliable OMDs fabrication.

It is noteworthy that along with the increasing molecular conjugation, the molecular memory type changes obviously from FLASH to WORM, which holds promise to realize different functionalities in information storage. Besides, as the molecular conjugation rises, the SET voltages ( $V_{SET}$ , i.e., the switching voltage of the memory device at which the device switches from LCS to HCS) of these devices become more narrowly-ranged (Fig. S11†), which is in good accord with the

morphological improvement from **NIBe** to **NIPy**. The highquality and homogeneous films help reducing the series contact resistances between the organic layer and top/bottom electrodes,<sup>49,50</sup> and thus leading to reproducible behaviors over large areas. Simultaneously, we have examined the stabilities of these dip-coated OMDs through retention time test under a constant stress of -1.0 V. No unfavourable degradation of these devices in both LCS and HCS is detected for at least 1×10<sup>4</sup> s (Fig. S12†), which shows that these devices are endurable under external voltage stress and possess stable NVM nature.

#### **Resistive Memory Mechanism Discussion**

It has been reported that the metal electrode could have an influence on the performance of memory devices (e.g., metal

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filament conduction).<sup>1,20,51</sup> To investigate this possibility, we altered the top Al electrode into inert gold (Au) and fabricated memory devices with ITO/small-molecule/Au structure. The electrical characteristics of these memory devices were measured under the same condition (Fig. S13†), which are similar with those shown in Fig. 8. Together with the good stability and the structure-dependent memory performance of the devices, it can be concluded that the electrical transitions are intrinsic to the organic small molecules.<sup>23</sup>

To get insight into the underlying memory mechanisms of NIBe, NIQu and NIPy, density functional theory (DFT) calculations were performed to further understand their electrical properties. The molecular electrostatic potential (ESP) isosurfaces (Fig. 9) show that the continuous positive ESP (in yellow-green) occurs throughout the molecular surfaces, forming an open channel, where the charge carriers can transport smoothly. Yet, the negative ESP region aroused from the electron-deficient NI acceptor (in blue) also exists, which could act as "charge trap" to impede the charge migration.<sup>21,52</sup> The electron affinities of NIBe, NIQu and NIPy are determined to be quite similar (~3.0 eV), which attributes to the same electron-withdrawing NI acceptor. Besides, the dihedral angles between the NI unit and the acene specie are found to be around 54°-55°, which might result in charge injection barrier.<sup>53</sup> Under a low voltage bias, charge carriers can hardly get enough energy to overcome the injection barrier between the acenes and NI acceptor. Thus, the device stays in the LCS. When the bias increases, the charge carriers gradually acquire sufficient energy and inject from the acenes to NI part to fill the trap, leading to the LCS-to-HCS switching with "trap-free" environment.

Moreover, the calculated HOMO and LUMO of NIBe, NIQu and NIPy were also shown in Fig. 9. As noted, the HOMO and LUMO surfaces were unevenly distributed. The electrons of HOMOs are mainly-distributed over the acene part, while the electrons of LUMOs are located at the NI acceptor side. The calculated HOMO-LUMO band gaps were 2.16, 1.89 and 1.83 eV for NIBe, NIQu and NIPy, respectively. These electron distributions indicate the NI-trap-induced intra-molecular charge transfer (ICT) under electric field.<sup>23,54</sup> However, it can be noted that as the molecular conjugation increases from NIBe to NIPy, the distance between the HOMOs and LUMOs increases accordingly. For NIBe, the HOMOs and LUMOs are partly overlapped at the NI side. Due to the overlap and short distance between the HOMOs and LUMOs, the trapped charges by NI acceptor can be easily de-trapped to the original state under a reverse voltage bias,<sup>55</sup> thus FLASH-type memory behavior was observed. For NIQu, such HOMOs/LUMOs distance relatively increases, which makes the charge recoverable process become difficult. As a result, the recovered FLASH-type ratio of NIQu-based device decreases. When it comes to NIPy, the distance between the HOMOs and LUMOs further extends to be larger than NIBe and NIQu. The HOMOs and LUMOs are well-separated and exhibit few overlap. Thus, the trapped charges could be facilitated by the ICT process to form a stable charge-separated state.<sup>20,54</sup> This charge-separated state could not be easily recovered to the

initial state under reverse voltage bias. Therefore the NRy based device shows unrecoverable  $WORM^{1}$  is  $VORM^{1}$  in the shows unrecoverable  $WORM^{1}$  is the shows performance.

#### Conclusions

In summary, we have demonstrated dip-coating as a facile, versatile and efficient technique to prepare high-performance OMDs and gain precise control over molecular self-assembly. Compared to the spin-coating method, dip-coating successfully induces the morphological evolution, which produces highquality and homogeneous nanopatterns over large areas. As a result, the corresponding solution-processed OMDs through dip-coating method exhibited far superior performances and stability. As far as we know, this is the first report about dipcoated OMDs with uniform device reproducibility as high as 96%, which opens a new pathway for fabricating highlyefficient organic memories in large-scale control. Further studies on the versatility of dip-coating method for other functional materials based OMD systems over both rigid and flexible substrates, and the fine tuning of their self-assembly behaviors are now in progress.

#### Experimental

**Optimal Dip-Coated Films Preparation and OMDs Fabrication** The ITO-coated glass substrates (2×2 cm<sup>2</sup>) were cleaned sequentially with distilled water, acetone, and ethanol by ultrasonication. NIBe, NIQu and NIPy were dissolved in ODCB (Aldrich 99%, anhydrous) to form 10 mg/mL solution, respectively. Then the ITO substrates were vertically immersed into the organic solutions and pulled out at a constant rate of 10 µm/s. Dip-coating was performed in an airtight box on a shock-absorbing stage to eliminate the effects of air flow, mechanical vibrations, and noise (temperature = 20-25 °C, humidity = 35-60%). Afterwards, the top AI electrode with thickness of about 100 nm was thermally deposited onto the organic dip-coated films through a shadow mask with circular patterns. The active area of the target memory device cell was 0.126 mm<sup>2</sup> (a nummular Al electrode pattern with radius of 0.2 mm). Under ambient laboratory condition, current-voltage measurements of the non-packaged OMDs were implemented using a Keilthley 4200-SCS semiconductor characteristic system. During the device measurement, the top and bottom electrodes of the OMDs were attached to the terminals of Keilthley 4200-SCS instrument, respectively. Under the voltage sweeping mode, voltage bias was applied to the device at a normal speed without sweep delay. The sweep step of the current-voltage characteristics was 0.05 V, and the compliance current was 0.1 A (Table S2<sup>†</sup>).

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### **Controlled deposition of large-area and highly-ordered thin films: effect** 1.05.1039/C9TC00431A dip-coating-induced morphological evolution on resistive memory performance

Yang Li,<sup>\*,a,b,c</sup> Cheng Zhang,<sup>b</sup> Zhuang Li,<sup>b</sup> Peiyang Gu,<sup>c</sup> Zilong Wang,<sup>c</sup> Hua Li,<sup>\*,b</sup> Jianmei Lu,<sup>\*,b</sup> and Qichun Zhang<sup>\*,c</sup>

#### Table of Contents



A scalable dip-coating technique is reported to precisely control nano-patterned films and resistive memory devices with a record reproducibility (96%).