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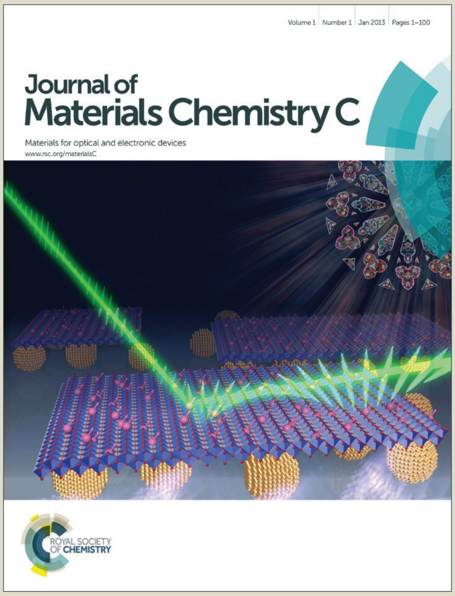

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ARTICLE

Recent Progress on Organic Resistance Memory with Small Molecules and Inorganic-organic Hybrid Polymers as Active Elements

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The organic resistance memory has attracted a lot of attentions due to its high scalability, flexibility, easy processing, low fabrication cost, etc. Organic small molecules, which own well-defined structures and more accurate experiment-simulation matching, have been widely explored as the active materials for the application in organic resistance memory. In addition, inorganic-organic hybrid polymers have been expected to have charming resistive switching properties because they can potentially combine the advantages of both inorganic materials and organic polymers. This review presents the recent progress of organic resistance memory based on several families of organic small molecules and some typical inorganic-organic hybrid polymers, and the discussion on their structure-property relationships.

1. Introduction

In the past decades, organic materials, including both small molecules and polymers, have been widely explored in organic sensors, organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), organic phototransistors, and organic photovoltaics (OPVs).[1-26] The high scalability, easy processing ability, flexibility, and low fabrication cost of organic electronics make them promising to be the next generation of electronics for commercial manufacture.[27-38] It is in high desire to expand the application of organic materials in new memory technology, namely organic resistance memory (ORM), which is expected to potentially own non-volatile ability, high switching speed, high data storage density and high cycling endurance.[39-46] Enormous efforts have been devoted in the investigation of novel organic materials in order to push forward the development of ORM from laboratory study to practical applications.

A typical ORM device has a sandwich architecture containing a layer of switchable material and two electrodes. Figure 1 shows the representative schematic graph and the active layer is clamped between two electrodes. The memory characteristics can be achieved by tuning the applied voltages, in which situation the resistance of active materials will change accordingly. Current-voltage (*I*-*V*) curves are generally used to characterize the memory behaviors. The key parameters used to evaluate the performance of ORM include: 1) the threshold voltage for SET (T_{SET}) and RESET (T_{RESET}) process, which are the voltages required to SET the device from high resistance state (HRS) to low resistance state (LRS) and RESET the device from LRS to initial HRS, respectively; 2) the ON/OFF ratio, which is the current ratio between LRS and HRS; 3) the endurance performance, which is the cyclic repeating ability for SET-READ-RESET-READ operation; and 4) the retention performance, which represents the stability of each switched state.[47-49] Basically, the memory behaviors are relative to the formation of filaments, the charge tunnelling effect, the filling of electron "traps" and the intermolecular charge transfer, etc.[50-52]

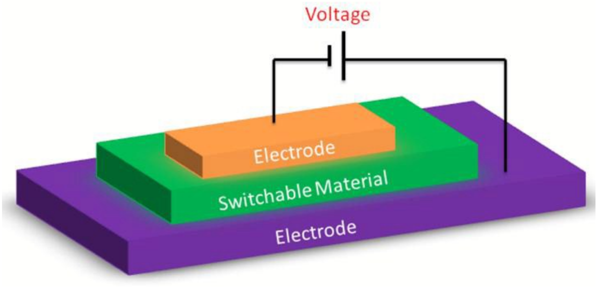

Figure 1 Schematic graph of the typical sandwich architecture memory device.

In fact, the study of memory effect of organic materials can be traced back to 1970s, when the polystyrene and Cu-TNCQ films were observed to switch between different resistance states.[53, 54] Since then, great progresses have been achieved. The well-defined structures of organic small molecules make them have good batch-to-batch reproducing ability in processing. In addition, the more accurate experiment-simulation matching of organic small molecules is favour for better understanding

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x of switching mechanisms.[30, 36, 55] Polymers, especially for inorganic-organic hybrid polymers, are expected to combine the advantages of both inorganic and organic materials.[56-58] This review covers the recent progress on organic small molecules and inorganic-organic hybrid polymers based ORM.

2. Organic Small Molecules for ORM

2.1 Azobenzene derivatives

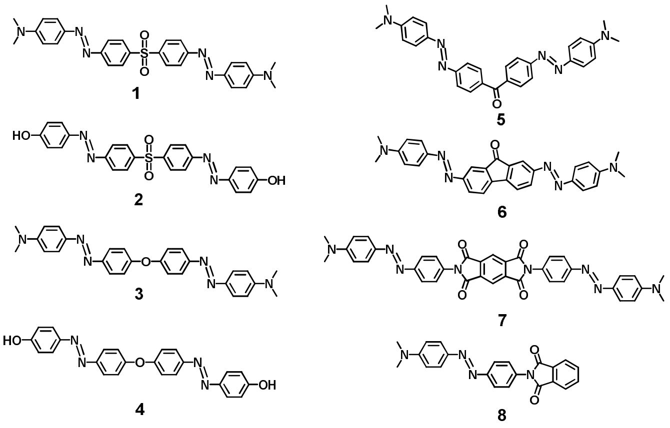

Figure 2 Molecular structures of representative azobenzene derivatives.

Li et al developed a series of azobenzene-based organic small molecules (**1**-**4** in Figure 2) with different centring and ending groups for ORM application since 2010.[30] The memory devices based on molecules **1**-**4** were fabricated through thermal evaporation method with ITO and Al as two electrodes, respectively. As shown in Figure 3a), compound **1** displayed three-state switching behavior, and the three states could be indexed as high resistance state (HRS), low resistance state 1 (LRS1, intermediate) and low resistance state 2 (LRS2, lowest resistance). Each state could maintain the as-switched situation in the bias-reading sweeping or even after removing voltage supply, suggesting the device was non-volatile. Once the device was switched to LRS1 from HRS or LRS2 from LRS1, it could not be recovered to the initial states, indicating that compound **1** was a write-once read-many-time (WORM) type memory material. LRS1 and LRS2 were reached step-by-step in SET process with the T_{SET} at -1.37 V and -2.09 V, respectively. The ON/OFF ratio of LRS2:LRS1 and LRS1:HRS were 10^6 and 10^2, respectively. The three states were well retentive, and there were no obvious current decay when a constant stress was applied for 10^3 s. Compound **2** showed no distinct memory properties while both **3** and **4** exhibited two-state memory behaviors with the T_{SET} at -1.7 V and -3.6 V, respectively. Theoretical calculations were carried out to understand the switching mechanisms for compounds **1**-**4**. As the authors proposed, these molecules **1**-**4** were designed with different numbers of donor and acceptor units (molecule **1**: one donor and two acceptors. It was believed that the various acceptor units in compound **1** (e.g. azo group and sulfone group) served as different electron "traps", which could be filled step-by-step to induce the three-state memory behaviors. Compound **1** was the first reported organic small molecule possessing multiple-state memory behaviors (more than two states). As illustrated in Figure 3b), the data storage capacity of the memory devices base on compound **1** was increased exponentially to 3^n. Clearly, the success of compound **1** could provide a novel strategy to develop ORMs with high density data storage ability.

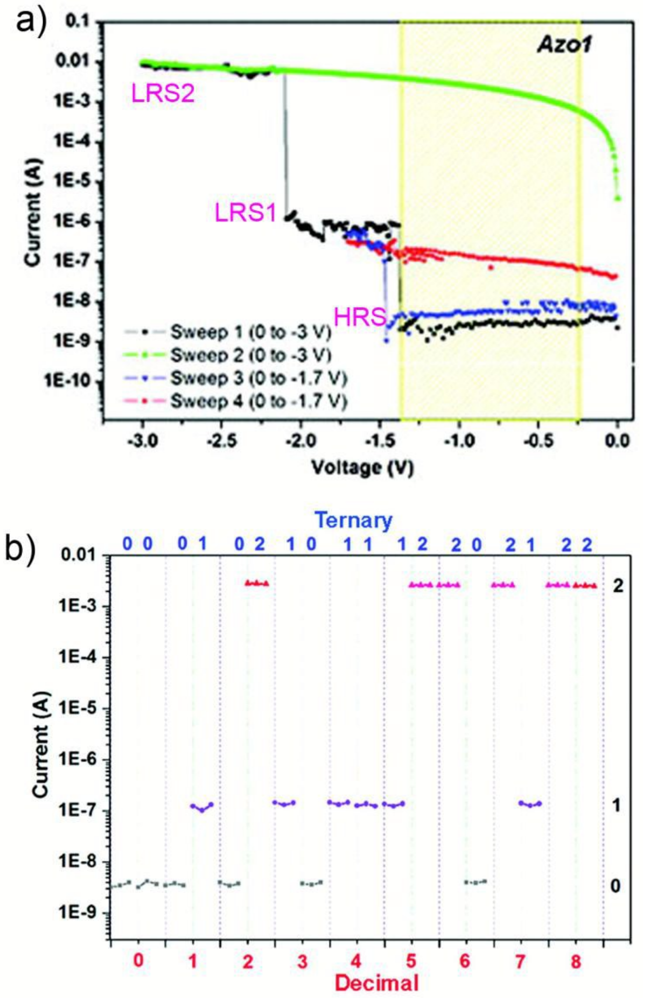

Figure 3 a) *I-V* curves and b) data storage capacity of memory device based on compound **1**. Reproduced from ref. 30. Copyright 2010 American Chemical Society.

Continuing on small-molecule-based memory devices, Miao et al from same group designed and synthesized two novel conjugated azobenzene molecules **5** and **6**, which had same terminal groups but different centre moiety comparing with compound **1**.[59] Based on density functional theory (DFT) calculation, compound **6** was predicted to have almost planar configuration while compound **5** possessed a twisted structure with a dihedral angle of 48.25°, and the difference might come from the change of centre moieties. The calculation suggested that these two compounds should have different packing modes in solid state. Employing the same method with compound **1**, the memory devices based on compounds **5** and **6** had been fabricated and both devices showed similar three-state WORM type memory behaviors. Each of the switched state was non-volatile with good retention ability (stable more than 10 h). Interestingly, the T_{SET} for compound **5** were -1.50 V and -2.61 V, while those for compound **6** were -1.05 V and -1.81 V, which were ~30% lower. Theoretical calculation indicated that compounds **5** and **6** had similar switching mechanisms with compound **1**. Cyclic voltammograms (CVs), atomic force microscopy (AFM), transmission electron microscopy (TEM), and X-ray diffraction (XRD) analysis based on the films and Forcite and CASTEP calculation for molecular packing investigation were carried out, and the results suggested that compound **6** had a lower hole injection energy barrier and more tight packing in solid state than compound **5** because of its more planar conformation, which could account for the lower T_{SET}. This work indicated that the rational designed planar molecules with different electron-withdrawing groups might be promising candidates for low power-consumption, high density data storage ORM materials.

Considering the length of molecules could be an effective factor to adjust the memory performance of organic small molecules, the Lu group designed two new compounds **7** and **8**. Note that compounds **7** and **8** have same electron-donating and electron withdrawing groups, but different structures (compound **7** has a symmetrical structure with doubled length compared with compound **8**).[60] The memory devices based on compounds **7** and **8** were fabricated in a similar method as for compounds **1**-**6**. Compound **7** exhibited three-state WORM type memory behavior with non-volatile ability and good retention performance while compound **8** showed no obvious memory characteristics. The evidence from the UV-vis absorption spectra, AFM and XRD analysis suggested that the longer molecule **7** had more orderly and compact packing in solid state while molecule **8** showed amorphous morphology in films. These results could be the reason why two compounds had big different performance in memory devices.

The multiple-state memory properties of the azobenzene derivatives mentioned above are all based on the mechanism that different electron-withdrawing groups can play various electron "traps". Thus, the key point to develop this type of materials is to combine multiple acceptor units in a single molecule. In addition, the planar molecules should have lower T_{SET}, which are promising as low power-consuming memory materials.

2.2 Oligoazaacenes derivatives

The electron-deficient oligoazaacenes[61] can be used as acceptor moieties to build up donor-acceptor (D-A) molecules, because conjugated oligoazaacenes could introduce multiple electron "traps" into as-designed molecules. It is well-known that oligoazaacenes derivatives have good stability and are more inclined to orderly stack in solid state, which will have a great contribution to better transportation of charge carriers. Based on these considerations, oligoazaacenes derivatives have been investigated as ORM materials by our group.

A series of D-A molecules with oligoazaacenes as acceptors have been developed by our group.[62-63] For example, compound **9** was integrated with a conjugated imidazole-[4,5-*b*]phenazine (**BIP**) moiety (acceptor) and triphenylamine (**TPA**) unit (donor), which had been widely used in memory materials due to its ability to stabilize the charge-separated state.[62a] Single crystal analysis of compound **9** suggested that it adopted offset intersection face-to-face stacking with a interlayer distance of 3.29 Å, which indicated that the molecule had compact orderly stacking in solid state as expected. The memory devices based on compound **9** was fabricated through spin-coating method with ITO and Pt as electrodes to avoid filamentary effect. As shown in Figure 5a), the device displayed two-state memory behavior with non-volatile ability. After the device was switched to LRS in SET process, it could be recovered to initial HRS in the reverse RESET sweeping, suggesting the device was rewritable. Generally, the device could be cyclically switched in SET-READ-RESET-READ operation up to 14 cycles. The average T_{SET} and T_{RESET} were 2.60 V and -1.45 V, and the ON/OFF ratio between LRS and HRS was 10^3. Each state could be well retentive for more than 4 × 10^3 s under a constant stress, suggesting the good retention performance of device.

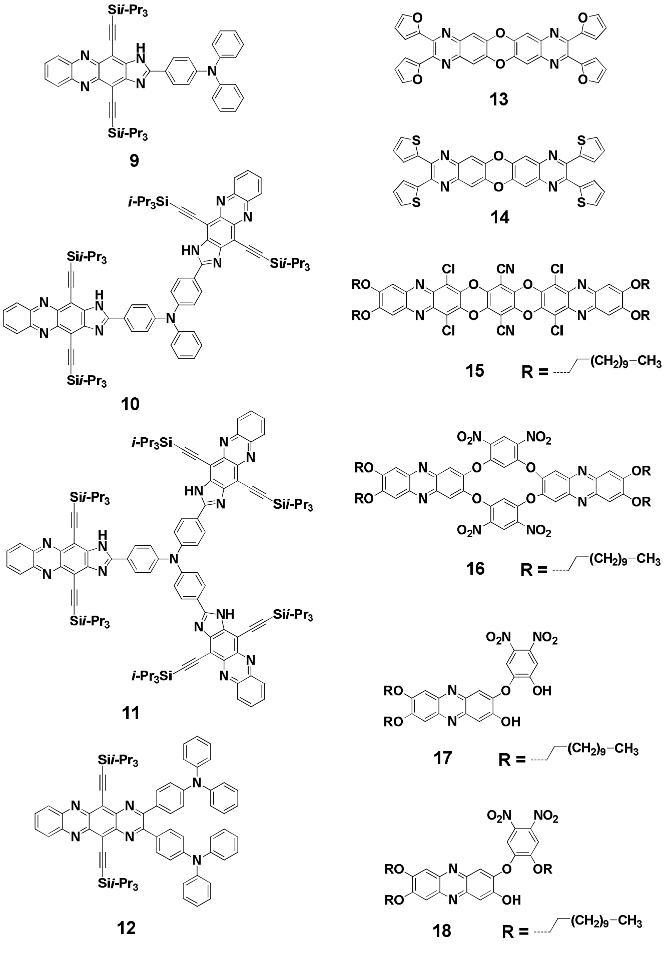

Figure 4 Molecular structures of representative oligoacenes derivatives.

The switching mechanism was demonstrated by theoretical calculation, which suggested that the **BIP** moiety might serve as electron ''traps'', and the filling of these "traps" could induce the change of resistance. Continuing on this work, two D-A molecules **10** and **11** have been synthesized with different numbers of acceptor moieties (2 acceptor moieties for **10**, 3 acceptor moieties for **11**), in order to investigate the influence of the number of acceptor moieties on the memory properties of molecules.[62b] The memory devices based on compounds **10** and **11** were fabricated in same method as described for compound **9**, except that Au was used as top electrode for more matching of energy levels. Both compounds **10** and **11** exhibited similar two-sate, rewritable, and non-volatile memory behaviors as mentioned for compound **9**. In a SET-READ-RESET-READ operation, both two compounds could be repeatedly switched for more than 100 cycles, suggesting their charming endurance performance, and besides, the HRS and LRS for the two types of devices could be retentive for more than 10^4 s. The average T_{SET} and T_{RESET} for compounds **10** and **11** were very close (0.83 V and -0.69 V for compound **10**, 0.84 V and -0.66 V for compound **11**) and much lower than that of compound **9**. Interestingly, the ON/OFF ratio of compound **11** was 10 times lower than that of compound **10** and the resistance distribution of 100 cycles was much narrower. The AFM analysis on the films of compounds **10** and **11** together with theoretical calculation indicated that increasing acceptor moieties did not generally affect the switching behaviors of molecules, while the change of molecular stacking in solid state could influence the ON/OFF ratio and the resistance distribution.

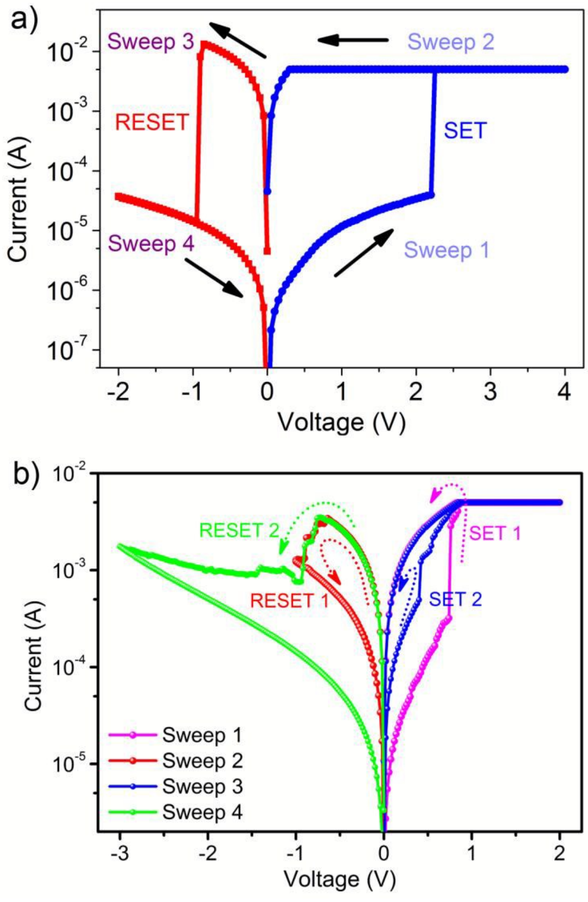

Figure 5 a) *I-V* curves for molecule **9**. Reproduced from ref. 61. Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA. b) *I-V* curves for molecule **12**. Reproduced from ref. 63. Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA.

Molecule **12** was designed by combing strong electro-deficient acceptor (5,12-bis((triisopropylsilyl)ethynyl)-1,4,6,11-tetraazatetracene) with multiple **TPA** donor units.[63] Compound **12** adopted offset intersection face-to-face stacking between neighbouring molecules in single crystals as well, but the interlayer distance was 3.626 Å, which was larger than that of common plane oligoazaacenes. In CV curves, two reductive peaks were observed, suggesting the existence of multiple redox behaviors of compound **12** when excited by voltage. The memory device based on compound **12** was fabricated in same method as described for compounds **10** and **11**, and the device exhibited three-state rewritable memory behaviors with non-volatility (Figure 5b)). Different with compounds **1**, **5**, **6**, and **7**, the intermediate LRS1 of compound **12** was achieved in RESET process by controlling the reverse sweeping voltage. LRS2 could be reached in SET1 or SET2 process from 0 V to 2 V sweeping, and LRS1 were obtained by a reverse RESET1 sweep from 0 V to -1.0~1.5 V, and a larger reverse RESET2 sweep from 0 to -3 V could produce HRS. Generally, the device could be repeatedly switched in SET1-RESET1-SET2-RESET2 operation for more than 70 cycles. The ON/OFF ratios between LRS2 and LRS1, LRS1 and HRS were ~8. All the HRS, LRS1 and LRS2 were well retentive for more than 10^4 s under constant stress. Theoretical calculation suggested that the unique memory property of compound **12** was probably induced by multiple electrons intermolecular charge transfer. The success of compound **12** might provide an efficient way to develop rewritable multiple-state ORM materials.

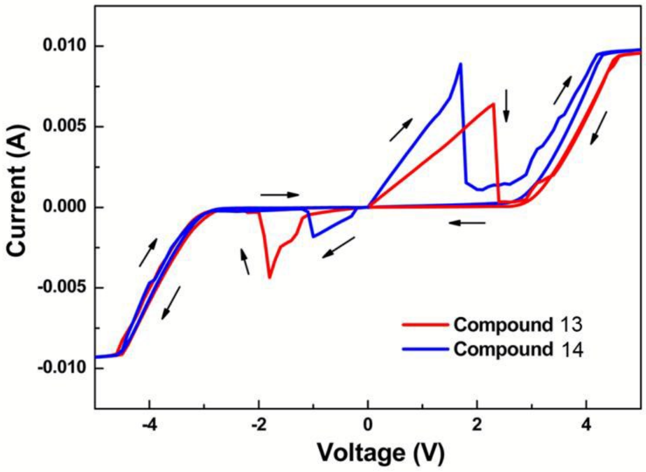

Figure 6 *I-V* curves of molecules **13** and **14**. Reproduced from ref. 64. Copyright 2013 American Chemical Society.

Conjugated oligoazaacenes have also been investigated as ORM materials. Compounds **13** and **14** were reported by Zhang et al in 2013.[64] The memory devices based on compounds **13** and **14** were fabricated by thermal evaporation method with ITO/**13** or **14**/LiF/Al architecture, and the 1 nm LiF was used as a buffer layer to decrease the interface energy barrier. As shown in Figure 6, both compounds **13** and **14** showed bipolar switching behaviors with non-volatile ability and good retention performance. Basically, the two types of devices could be switched for 10 cycles with an ON/OFF ratio of 10^2. Considering the near Ohmic conducting behavior of both compound **13** and **14** in LRS, the authors believed that the switching behaviors were originated from the formation of conducting filament. The instability of filaments under high voltage probably accounted for the unsatisfactory endurance performance of devices.

Oligoazaacenes **15** and **16** with large conjugated backbone containing different electron-withdrawing groups (pyrazine and cyano groups for compound **15**, pyrazine and nitro groups for compound **16**, respectively) were reported recently by our group.[65, 66] The memory devices based on compounds **15** and **16** were fabricated by same method as described for compounds **1**-**8**. Both compounds **15** and **16** exhibited three-state WORM type memory behaviors with non-volatile ability and good retention performance, which were similar to compounds **1**, **5**, **6**, and **7**. Theoretical calculations suggested that the switching behaviors came from the step-by-step filling of electron "traps" induced by different electron-withdrawing groups. These successes indicated that large conjugated oligoazaacenes could be promising high density data storage ORM materials. In another study, the influence of alkyl chains of molecules on their memory property was also investigated. Two small molecules **17** and **18** with same backbone but different alkyl substituents were designed.[67] The memory devices based on compounds **17** and **18** were fabricated in same method as for compounds **1**-**8**. Compound **17** exhibited three-state WORM type memory behavior with non-volatility and good retention performance, which was similar to compounds **1**, **5**, **6**, and **7**. However, compound **18** displayed only two-state WORM type memory characteristics. The UV-vis absorption spectra, AFM, XRD and theoretical calculation analysis indicated that the different memory behaviors of compounds **17** and **18** were attributed to the various molecular packing in solid states, which were induced by the change of alkyl chains. This discovery implied that in certain situation, adjusting alkyl substituents could tune the memory properties of molecules.

Intermolecular charge transfer of certain D-A molecules developed with oligoazaacenes as acceptor units can explain their memory behaviors, specifically multiple electrons transfer is proposed to induce rewritable multiple-state characteristics. One essential designing requirement for developing this type of materials is to combine strong electron-deficient acceptors unit with multiple donors.

2.3 Other Organic Small Molecules

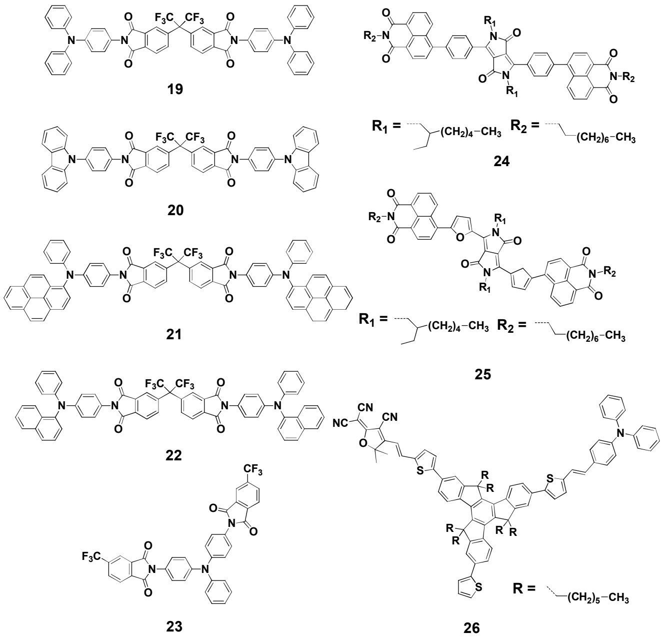

Figure 7 Molecular structures of other representative organic small molecules.

Chen group developed a series of small molecules (**19**-**23**) with different donor units and acceptor moieties for ORM application, which possessed various D-A structures.[50, 68] Compounds **19**-**22** had a D-A-D structure with **TPA**, carbazole, *N*-(4-aminophenyl)-*N*-phenyl-1-aminopyrene (**APAP**) or *N*-(4-aminophenyl)-*N*-phenyl-1-aminonaphthalene (**APAN**) as donor units, respectively, and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (**6FDA**) as an acceptor moiety. Compound **23** had an A-D-A structure with **TPA** as a donor and 4-trifluoromethylphthalic anhydride (**4TPA**) moiety as an acceptor. The memory devices based on these molecules were fabricated by same method described for compounds **1**-**8**. Compound **19** showed a negative-differential-resistance (NDR) memory behavior with non-volatile ability, in which situation the device was SET to LRS firstly and RESET to HRS in a single sweeping (Figure 8a). Basically, a 4 V voltage could SET the device to LRS and a 10 V voltage would recover the initial HRS. The ORM device could be cyclically switched for more than 20 cycles in SET-READ-RESET-READ operation with the ON/OFF ratio in range of 10^3~10^4. Under constant stress, both HRS and LRS could be retentive longer than 10^4 s. Compound **20** also displayed NDR memory behavior with non-volatility and good retention performance, which was similar to compound **19**. However, the ON/OFF ratio between LRS and HRS was only in range of 10^1~10^2. The authors believed that the planar and more rigid structure of carbazole had an important contribution to better transportation of charge carriers, hence the resistance in HRS of compound **20** was relatively lower, resulting in smaller ON/OFF ratio. The memory properties of compounds **21** and **22** were dependant on the thickness of active layer. When the thickness of active layer was 48 nm, both two types of devices showed NDR memory behaviors similar to compounds **19** and **20** with ON/OFF ratios around 10, which might also be explained by the planar and more rigid structure of **APAP** and **APAN** moieties. Theoretical calculation suggested that the charge “traps” played a crucial role in the NDR memory effects of **19**-**22**. Compound **23** showed no obvious memory characteristics. The big energy gap between the working function of Al and the LUMO level of compound **23** was proposed to account for difficult transportation of charge carriers, therefore **23** displayed no electrical bistability. The success of this family of organic small molecules might provide a useful strategy for developing novel ORM materials with D-A structure.

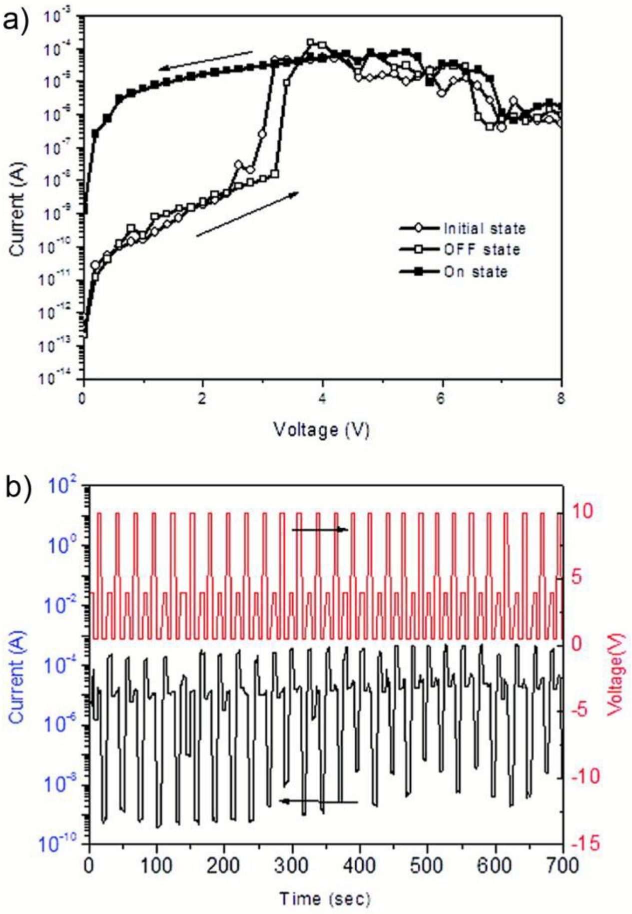

Figure 8 a) *I*-*V* curve and b) SET-READ-RESET-READ operation of ORM device based on compound **19**. Reproduced from ref. 50. Copyright 2013 American Chemical Society.

Lu team designed two diketopyrrolopyrrole-based small molecules (**24**-**25**), which utilized phenyl or furan groups as linking bridges to tune the planarity of molecular structure and crystallite orientation in solid states. Theoretical calculation found that compound **25** with furan unit as a linking bridge had a planar configuration. The ORM devices based on compounds **24** and **25** were fabricated by spin-coating method with ITO and Al as electrodes, respectively, and exhibited three-state WORM type switching behaviors with non-volatility and good retention performance. The same conclusion as their previous study referring to the effect of molecular planarity on T_{SET} was obtained, hence the average T_{SET} from HRS to LRS1 and from LRS1 to LRS2 of compound **25** was much lower with narrower distribution. The authors evaluated the reproducibility of memory characteristics for both molecules, and interestingly, in the statistic study of 100 devices, only 54% of compound 24 based devices showed the typical memory characteristics, while the ratio for compound **25** was 71%, suggesting that compound **25** had better memory property reproducibility in device processing. The AFM and XRD analysis confirmed that the good planarity and crystallite orientation in solid states of compound **25** played a crucial part for low power consumption and high device reproducibility.

Ye et al designed a D-bridge-A molecule **26**, with **TPA** as a donor, 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (**TCF**) as an acceptor, connected by a meta-conjugated bridge of a 2,7,12-trisubstituted truxene unit.[69] The memory device based on compound **26** was fabricated by a spin-coating method with ITO and Al as electrodes, respectively. As shown in Figure 9, the device exhibited two-state rewritable memory behavior under dark, however, it displayed three-state rewritable memory characteristics under UV light. Both types of memory behaviors were non-volatile with good retention performance. The T_{SET} and T_{RESET} under dark were at 2.0 V and –4.8 V, and those under UV light were 1.0 V, 1.7 V, - 3.4 and –5.2 V, respectively. In CV curves, the redox behaviors were well matched with the different memory characteristics under different conditions, in which there were only one oxidative peak under dark and two oxidative peaks under UV light. Theoretical calculation suggested that the different memory behaviors were induced by stepwise filling of electron “traps”. The success of this photo-inducing multiple states ORM molecule provided a new approach for developing high density data storage ORM materials.

NDR memory properties can also be observed in some D-A molecules. The molecular structure should have strong influence on their memory characteristics, i.e. ON/OFF ratio, etc. More importantly, the architecture of devices, especially the thickness of active layer play a key role to distinguish the unique NDR memory behaviors.

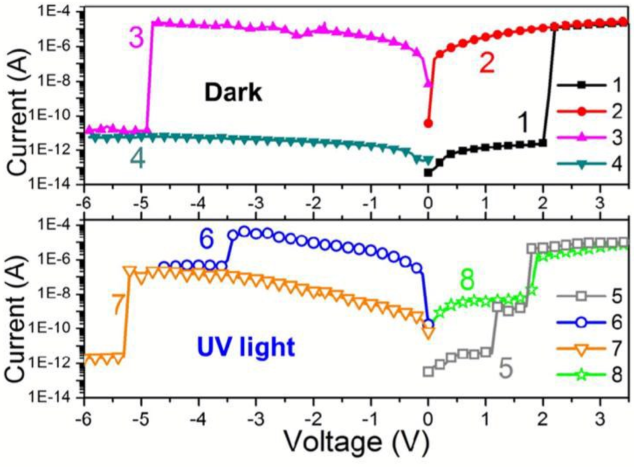

Figure 9 *I*-*V* curves for memory device based on compound **26**. Reproduced from ref. 69. Copyright 2012 American Chemical Society.

3. Inorganic-organic hybrid polymers for ORM

The inorganic materials such as chalcogenides and oxides have been investigated as resistance based memory materials as well, which own interesting endurance performance. In order to combine the advantages of both inorganic and organic materials together, inorganic-organic hybrid materials are proposed.

Yang and co-workers utilized polystyrene (**PS**) film containing 1-dodecanethiol-protected gold nanoparticles (**Au-DT NPs**) and 8-hydroxyquinoline (**8HQ**) as active layer and Al as both top and bottom electrodes to build up ORM devices, which could be solution-processed.[70] As shown in Figure 10a), the device represented in form of Al/**Au-DT+8HQ+PS**/Al showed two-state rewritable memory characteristics with non-volatile and good retentive properties. By SET-READ-RESET-READ operation, the device could be repeatedly switched for numerous cycles with ON/OFF ratio at ~10^2. It was believed that the memory effect could be attributed to the electric-field-induced charge transfer between the **8HQ** and the **Au-DT NPs**.

Biological materials were also investigated by Tseng et al, who incorporated Pt nanoparticles with tobacco mosaic virus (**TMV**). The hybrid system **TMV-Pt** was solution-processable in polyvinyl alcohol (**PVA**) matrix, and the memory device was fabricated in Al/**TMV-Pt**/Al structure.[71] Similar with other composite materials, the device showed two-state rewritable memory characteristics with non-volatility (Figure 10b)). Charming endurance performance was observed, and in a SET-READ-RESET-READ operation, the device could be repeatedly switched for more than 400 cycles. Al/**TMV-Pt**/Al device showed temperature-dependant retention performance, and at 250 K, it could maintain its stability more than 10^4 s. The switching mechanism of the Al/**TMV-Pt**/Al device was attributed to charge trapping in Pt nanoparticles and charge tunnelling effect. Incorporating nanoparticles with biomolecules opened up new possibilities for developing novel ORM materials.

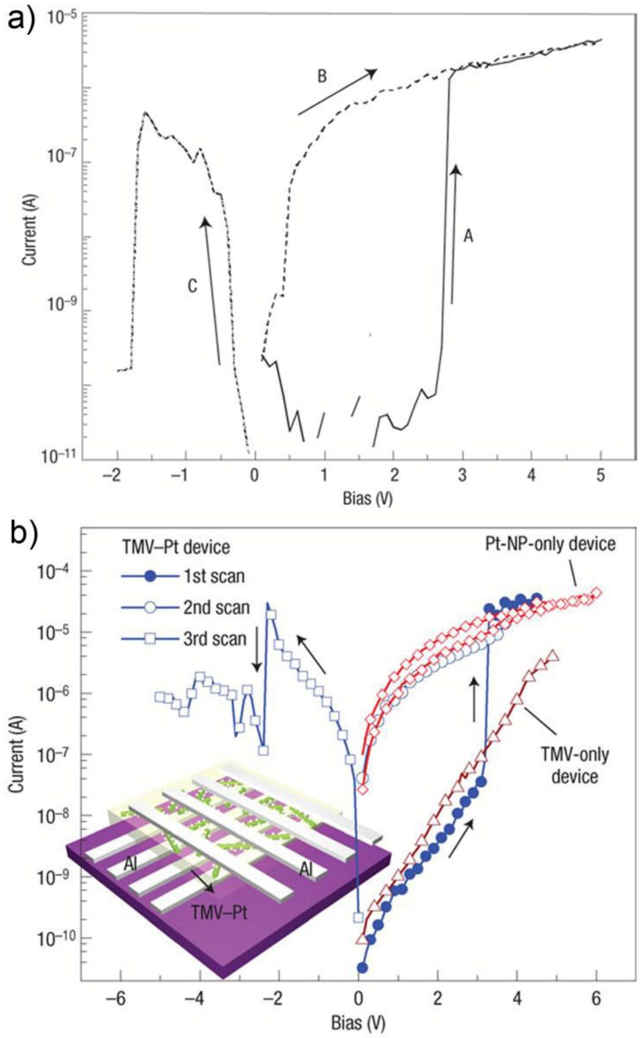

Figure 10 a) *I-V* curves of **Au-DT+8HQ+PS** based ORM devices. Reproduced from ref. 70. Copyright 2004 Nature Publishing Group. b) *I-V* curves of **TMV-Pt** based ORM devices. Reproduced from ref. 71. Copyright 2006 Nature Publishing Group.

Tseng et al also developed polyaniline nanofiber (**PAN**)/gold nanoparticles (**Au-NPs**) composite system as memory material.[72] Figure 11a) illustrates the TEM image of the **PAN**/**Au-NPs**, suggesting that the **Au-NPs** (~1 nm) have been successfully attached on the surface of **PAN** wires (~30 nm diameter). The device based on **PAN**/**Au-NPs** was fabricated by spin-coating method with Al as electrodes. The Al/**PAN**/**Au-NPs**/Al device exhibited two-state rewritable memory characteristics with non-volatile ability, and it could be cyclically switched for many times in SET-READ-RESET-READ operation. It was noteworthy that **PAN**/**Au-NPs** composite owned excellent retention property, and each of the switched state of Al/**PAN**/**Au-NPs**/Al device could be stable in laboratory conditions for 3 days.

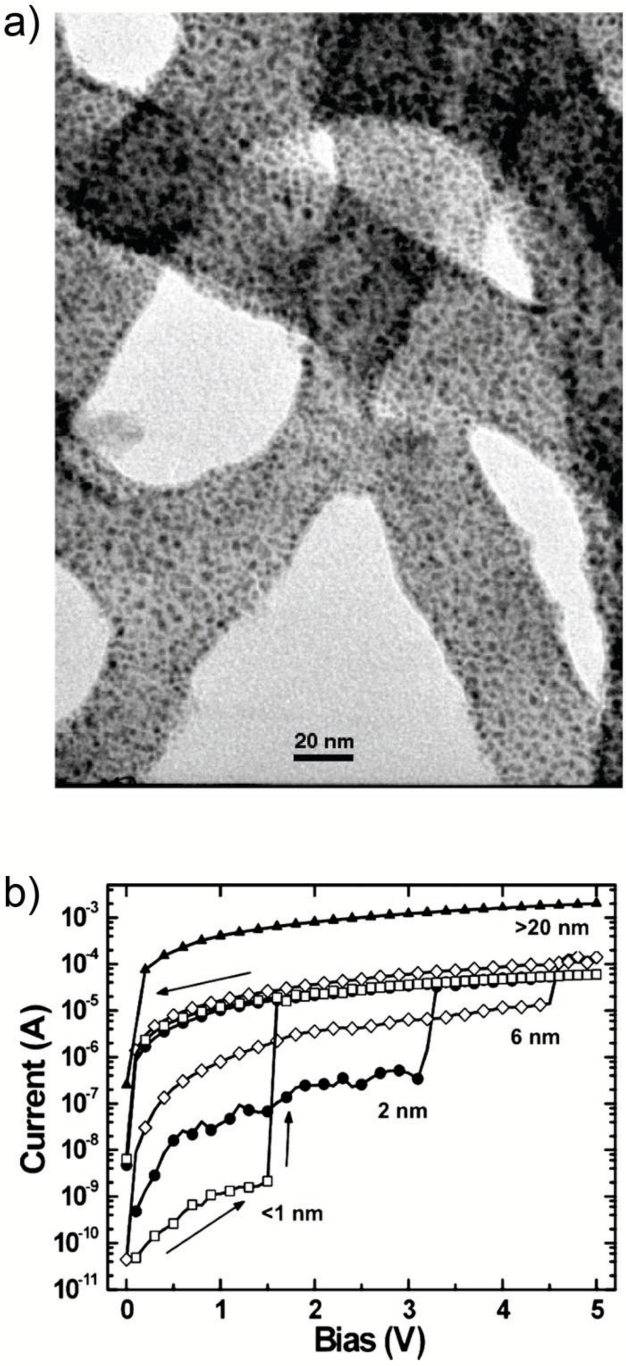

Figure 11 a) TEM image of the **PAN**/**Au-NPs** composite. Reproduced from ref. 72. Copyright 2005 American Chemical Society. b) *I-V* curves of the corresponding devices with different nanoparticle size. Reproduced from ref. 56. Copyright 2011 American Chemical Society.

Continuing with this work, Baker et al studies the effect of the size of **Au**-**NPs** on the memory behaviors of Al/**PAN**/**Au**-**NPs**/Al device in 2011.[56] Figure 11b) shows the *I-V* curves corresponding to the **Au**-**NPs** size < 1, 2, 6 and > 20 nm, respectively. As the size of **Au**-**NPs** increased, the T_{SET} increased but the ON/OFF ratios decreased accordingly, which could be accounted by the less charge trapped in HRS and lower barrier from the close proximity of smaller **Au**-**NPs**. 2 nm **Au**-**NPs** composite gave the best memory performance with low T_{SET}, high ON/OFF ratio and excellent endurance performance which could be cyclically switched in hundreds. The switching behavior in **PAN**/**Au**-**NPs** composite might be relevant to the electric-field-induced charge transfer between the **PAN** and the **Au**-**NPs**.

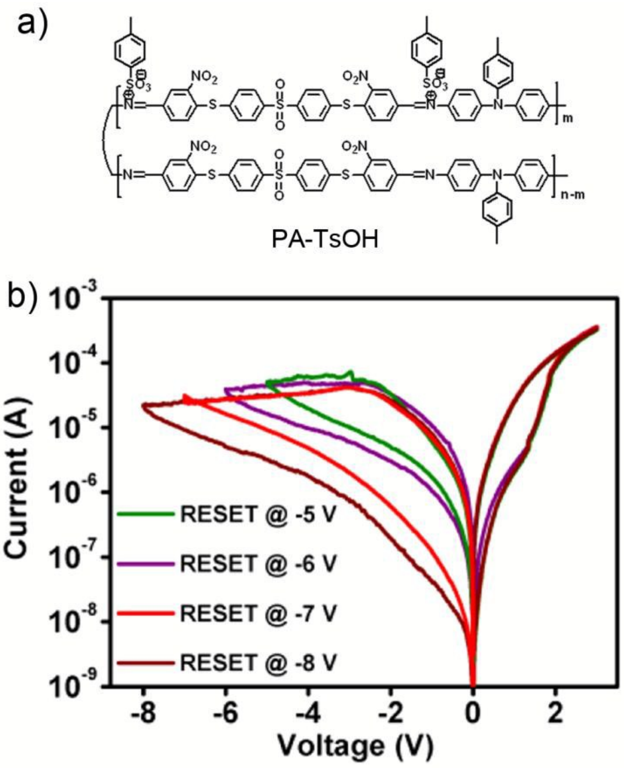

Figure 12 a) The structure of **PA-TsOH**. b) The *I-V* curves of **PA-TsOH** based ORM device. Reproduced from ref. 31. Copyright 2012 American Chemical Society.

The ion-doped conjugated polymers have also been investigated as ORM materials. Li group reported a *p*-toluenesulfonic acid (**TsOH**) doped poly-azomethine (**PA**) and studied its switching properties.[31] Figure 12a) shows the structure of **PA**-**TsOH,** in which **TsOH** mainly reacted with the azo groups. The ORM device with Pt/**PA**-**TsOH**/Pt architecture was fabricated by spin-coating method, and it exhibited multiple-state rewritable memory characteristics with non-volatility. The multiple memory states were generated by controlling the RESET voltage, and the cyclic switching between these states could be repeated for more than 700 times with good uniformity, which indicated its charming endurance performance. However, all the LRSs could not be retentive for long time. The resistance-switching effects of **PA**-**TsOH** might be relative to the electric-field induced doping/de-doping process.

Polyoxometalates (**POM**s) have proven to be soluble semiconducting oxides with multiple redox states.[73-76] Recently Zhang et al incorporated **POM**s with methyl methacrylate (**MMA**) to build up a hybrid polymer (**PMMA**-**MAPOM**), which was expected to own multiple states redox behaviors and easy processibility.[77] The memory device based on **PMMA**-**MAPOM** with ITO and Pt as electrodes was fabricated by spin-coating method, and it exhibited three-state rewritable memory behavior with non-volatile ability. The intermediate LRS1 state was produced by applying suitable RESET voltage, and the device could be repeatedly switched between the three states for about 20 cycles. Each switched state could be retentive for more than 10^4 s when applying a constant stress in laboratory conditions. The multiple states switching behaviors of **PMMA-MAPOM** were attributed to the change of the density of charge carriers resulting from the different redox states of manganese centres under various voltages. This success suggested that hybrid polymers could be promising candidates to develop multiple states ORM materials.

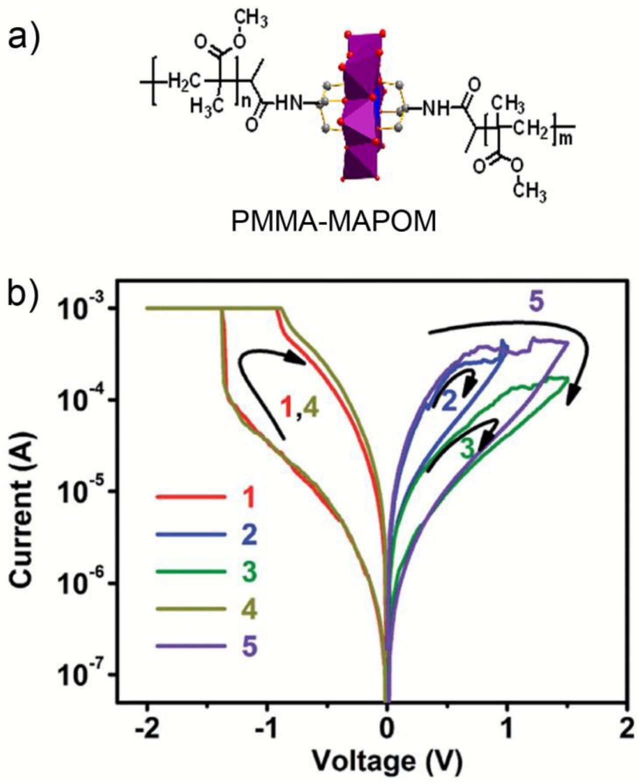

Figure 13 a) The structure of **PMMA-MAPOM**. b) The *I-V* curves of **PMMA-MAPOM** based ORM device. Reproduced from ref. 77. Copyright 2014 Royal Society of Chemistry.

4. Conclusions

This review presents the recent progress of some representative organic small molecules, including azobenzene based derivatives, oligoazaacenes and other small molecules and inorganic-organic hybrid polymers in the application of ORMs. The concerned highlights cover the designing strategies of these materials, the memory characteristics of the corresponding devices and the switching mechanisms. Besides, the structure-property relationships are illustrated, referring to the arrangement of donor and acceptor units, molecular length, alkyl substituents and planarity of molecules, etc. To date, great improvements have been achieved especially for the development of multiple-state memory materials to realize high density data storage. However, there is still a long way to reach the ultimate ORM, whose key limitation is the relatively poor endurance performance. Novel materials with good stability and solubility, and particular structure, i.e. multiple acceptor units or strong electron-deficient acceptor, are highly desirable to address the challenge. In addition, the device engineering including the choice of electrodes and the control of the thickness of active layer is another future focus.

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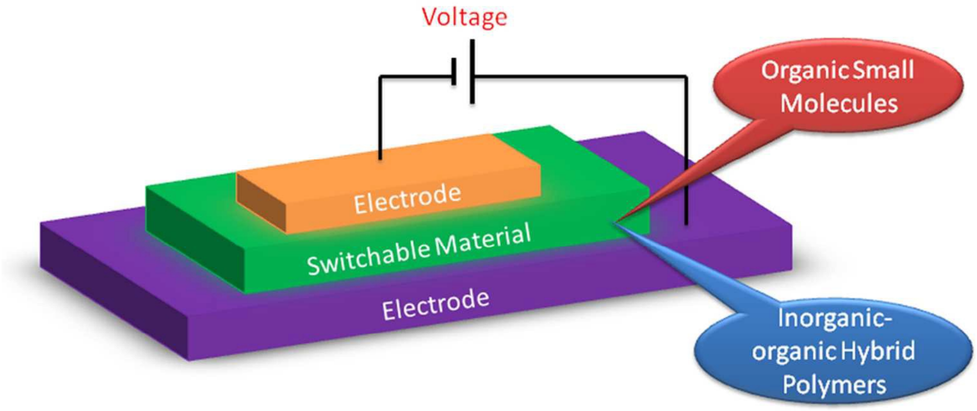

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