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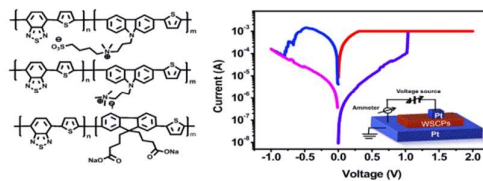
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Organic Nonvolatile Memories Processed from Water-soluble Donor-Acceptor Polymers

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Memory devices based on three water-soluble donor-acceptor conjugated polymers are fabricated from aqueous solution, and show excellent memory performance.

Keywords: resistance switching, nonvolatile memory, water-soluble polymer, ecofriendly fabrication

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Water-soluble Conjugated Polymers as Active Elements for Organic Nonvolatile Memories

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The eco-friendly solvents are very important in the green fabrication of organic electronic devices. However, such efforts on organic nonvolatile memories (ONVMs) are rare. In this article, three water-soluble donor-acceptor conjugated polymers (WSCPs) have been synthesized, which are used as switching layer to prepare ONVM devices with water as a solvent. The as-fabricated memory devices show large ON/OFF ratios, good endurance and long retention. Our success could provide a green way to fabricate high-performance organic non-volatile memories (ONVMs).

Introduction

Since the discovery of semiconducting polyacetylene in 1977, soluble conjugated polymers have become an important type of organic materials due to their solution processability, mechanical flexibility and lightweight. These charming advantages have endowed them the priority for the applications in organic light-emitting diodes (OLEDs), organic thermoelectric, organic thin-film transistors (OTFTs), organic photovoltaics (OPVs), and organic non-volatile memories (ONVMs).¹⁻³ Among these applications, ONVMs have attracted many scientists as a rising star because of their potential for the next-generation high density data storage.⁴⁻⁶ In the past decade, a lot of efforts have been input to investigate novel materials and device architectures to approach large ON/OFF ratio, good endurance, long retention time, low power consumption, fast switching speed, and excellent uniformity of operating parameters of ONVMs.^{2,7-9} Especially, the gradual uncovering of switching mechanism of ONVMs is accelerating their practical applications in manufacture.^{8,10,11}

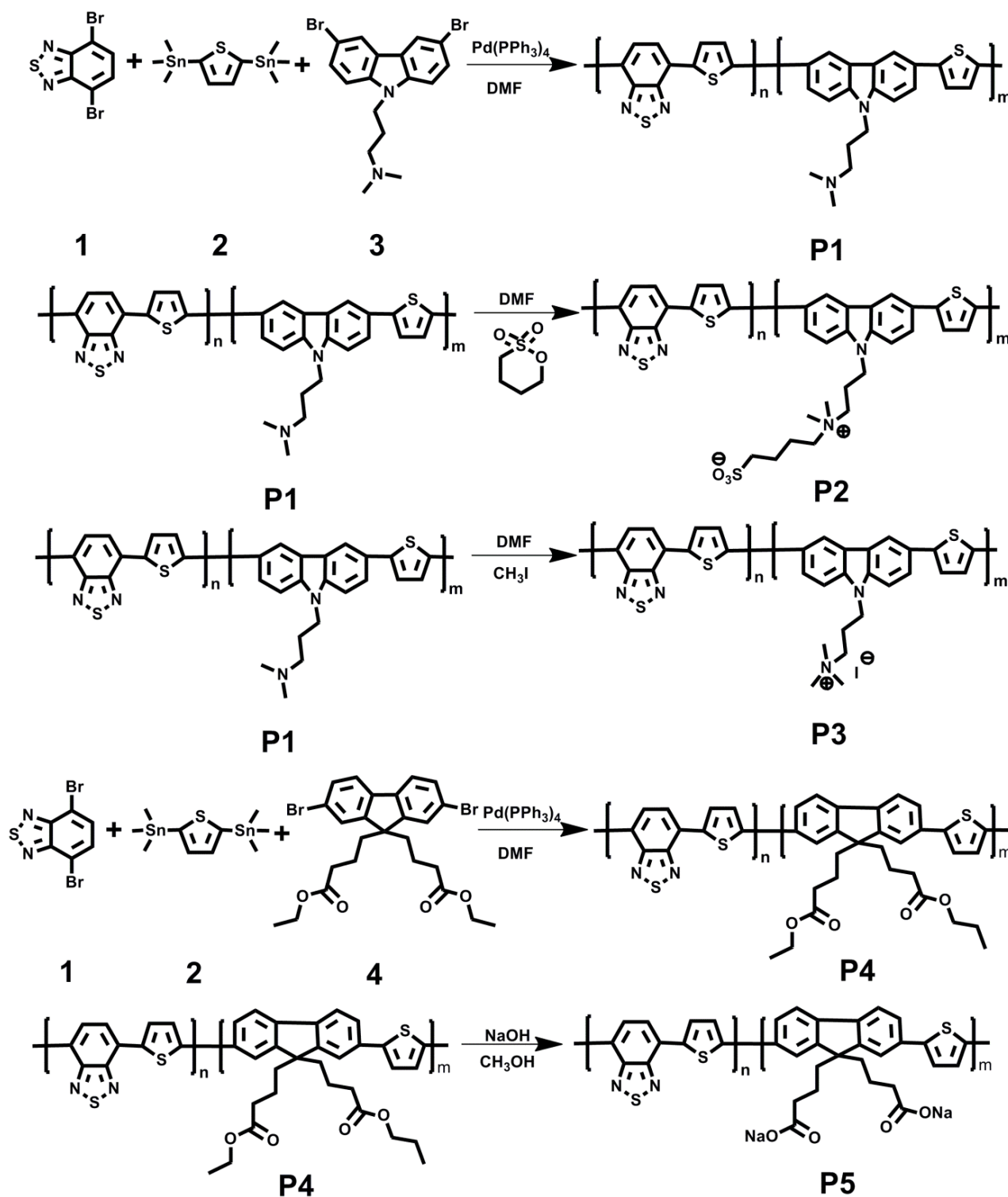
Unfortunately, the common solvents used for the fabrication of ONVM devices are halogenated aromatics and/or alkanes such as chlorobenzene, dichlorobenzene and cyclohexanone, which are toxic and not environmentally-friendly.^{3,12} It is believed that these solvents have strong negative impact on human health due to their potential carcinogenicity. Moreover, from the perspective of high throughput industrial manufacturing, it is very expensive and energy-consuming to produce these solvents. In addition, the involving of these toxic solvents during fabrication strongly requires a complicated procedure to operate the processing equipment. Thus, replacing toxic organic solvents to cheaper and less harmful alternates is

highly desirable. Although the replacement of toxic solvents has been explored in the fabrication of OFETs, OPVs and OLEDs,¹³⁻¹⁵ such efforts on ONVMs are rare. Therefore, it is highly on demand to search more environmentally-friendly solvents for the fabrication of ONVMs.

In recent years, water-soluble conjugated polymers (WSCPs) have attracted particular interest in organic electronics because they are ready to be processed from environmental-friendly solvents (such as water, alcohols etc.), which well meet the requirements for green fabrication.¹⁵ Compared to conventional conjugated polymers, WSCPs have several advantages for their promising applications in organic electronic devices: (i) the processing are more eco-friendly since water is a green solvent, (ii) because water involves in the fabrication process, the devices should have no moisture-driven degradation problem leading to an improved stability under ambient conditions, (iii) the performance of devices could be strongly improved by effectively enhancing charge injection through the reduction of the work function of conductor electrodes.^{14,15}

In this contribution, we report a series of water-soluble D-A polymers that can be employed as active elements in resistance memory devices with excellent performance. Three types of WSCPs including cationic, zwitterionic and anionic have been designed and prepared for memory devices. In typical WSCPs, carbazole unit and fluorene unit are used as donors and benzothiadiazole unit is employed as an acceptor. The as-prepared WSCPs with different polyelectrolyte types and different donors/acceptor showed excellent resistance memory effect. Our success could provide a green way to fabricate high-performance ONVMs. To the best of our knowledge, this is the first report to employ water as a solvent to fabricate ONVMs, which may pave the way to manufacture ONVMs greenly.

Scheme 1. The synthetic route to water-soluble D-A polymers



Results and discussion

The synthesis route is shown in **Scheme 1**. The monomers **3** and **4** were synthesized through the reaction between 3,6-dibromocarbazole and 3-dimethylaminopropylchloride

hydrochloride or between 2,7-dibromofluorene and ethyl 4-bromobutyrate, in a mixture of $\text{H}_2\text{O}/\text{DMSO}$ in the presence of excess NaOH with tetrabutylammonium bromide as a phase transfer catalyst according to literatures.^{16,17} The neutral polymers were synthesized by Stille coupling polymerization.

To enhance the solubility of the final polymers in water, no long side chain is incorporated into monomers **1** and **2**. As expected, the neutral polymers (**P1** and **P4**) can be just soluble in strong polar solvents such as dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and *N*-Methyl-2-pyrrolidone (NMP). The WSPC **P2** and **P3** were obtained by the quaternization between **P1** and iodomethane or 1,4-butane sultone; and WSPC **P5** was obtained by the hydrolysis of neutral carboxylate-containing polymer **P4**. The chemical structure of neutral polymer **P1** and quaternized polymers **P2** and **P3** were characterized by ^1H NMR (Figure S1) and FT-IR (Figure S2) to confirm the successful functionalization of side chain. Due to the poor solubility, the neutral **P4** and hydrolyzed product **P5** were characterized by FT-IR, which shows the carbonyl peaks (1730 and 1080 cm^{-1} , $-\text{COOC}_2\text{H}_5$) and carboxylate ion peaks (1630 , 1550 and 1410 cm^{-1} , $-\text{COONa}$).

After quaternization, the resulted WSPC **P2** and **P3** are insoluble in THF and chloroform but completely soluble in polar solvents such as DMF, DMSO, NMP and water. The solubility of **P2** and **P3** (powders) in water can reach to 20 mg/mL . However, the solubility of polyanionic polymer **P5** (powder) is different from that of quaternized polymers **P2** and **P3**. After the hydrolysis of neutral polymer **P4**, evaporating all solvents, and dialysis with pure water, an aqueous solution of **P5** with a concentration of $\sim 0.5\text{ mg/mL}$ was obtained. Although the aqueous solution of **P5** can be concentrated to $\sim 50\text{ mg/mL}$ without any precipitate more than one month, however, after removing all solvents at 80°C , the obtained powder became insoluble in water. Therefore, in order to solve the fabrication problem, a concentrated aqueous solution (20 mg/mL) after dialysis was directly used for UV-vis measurement and the fabrication of memory devices while the black powder of **P5** was used for FT-IR, TGA and DSC testing. The neutral polymers **P1** and **P4** have good thermal stability with degradation temperatures ($T_{d10\%}$) at 271 and 361°C , respectively (Figure S3). Compared with their neutral precursors, the thermal stabilities of the polyelectrolyte **P2**, **P3** and **P5** are slightly decreased. The glass transition temperature range of **P1-P5** is $85\text{--}101^\circ\text{C}$, as shown in Figure S4. The TGA and DSC results confirmed that the as-prepared water-soluble polymers are thermally stable, which should have their own applications in microelectronics industry.

Figure 1a shows the UV-vis absorption spectra of five polymers in DMF or water with a concentration of $\sim 1 \times 10^{-5}\text{ M}$ based on the repeat units of polymers. Both neutral polymers **P1** and **P4** in DMF show two absorption bands. The absorption peak at 357 nm for **P1** (or at 423 nm for **P4**) is attributed to fluorene (carbazole) segments while the absorption peak at 540 nm for **P1** (or 547 nm for **P4**) may come from the intramolecular charge transfer between the donors fluorene/carbazole units and the acceptors benzothiadiazole units. The optical band gaps of **P1** and **P4** are estimated to be 1.88 eV and 1.80 eV from the onset optical absorbance of 660 nm 690 nm , respectively. Compared with their corresponding neutral polymers, the absorption of **P2**, **P3** and **P5** is slightly redshifted, especially for the absorption bands of **P1** and **P4** in the range of $500\text{--}600\text{ nm}$, while the corresponding bands of **P2**, **P3** and **P5** show obviously redshift with $20\text{--}40\text{ nm}$, which may be due to the aggregation of the polymer chains through hydrophobic $\pi\text{--}\pi$ stacking interactions and electrostatic attraction among the ions at the sidechain.¹⁸

The electrochemical behaviours of all polymer films (coated on platinum plates) using 0.1 M solution of

tetrabutylammonium tetrafluoroborate ($n\text{-Bu}_4\text{NPF}_6$) in anhydrous dichloromethane were investigated by cyclic voltammogram (CV, in Figure 1b). Two groups of reduction waves can be observed in **P1-P3**. The first oxidation peak occurred at $\sim 1.1\text{--}1.6\text{ V}$ and the corresponding first-reduction peak occurred at $\sim 1.1\text{--}1.4\text{ V}$, respectively. These peaks can be attributed to the oxidation and the reduction of the terminal amino or ammonium groups. The second oxidation and reduction peaks of **P1-P3** are observed at $1.6\text{--}2.0\text{ V}$ and $\sim 1.90\text{ V}$, which can be attributed to the oxidation and the reduction of polymer chains.^{13c} For **P4**, a pair of oxidation and reduction peaks can be observed at $\sim 1.6\text{ V}$ and -1.5 V , which are the redox features of polyfluorene mainchains. The peak at $\sim -1.80\text{ V}$ may come from two ester groups because it disappeared in the hydrolyzed product **P5**.^{17,18} After hydrolysis, the water-soluble **P5** show two new oxidation peaks at $\sim 1.4\text{ V}$ and $\sim 1.9\text{ V}$.

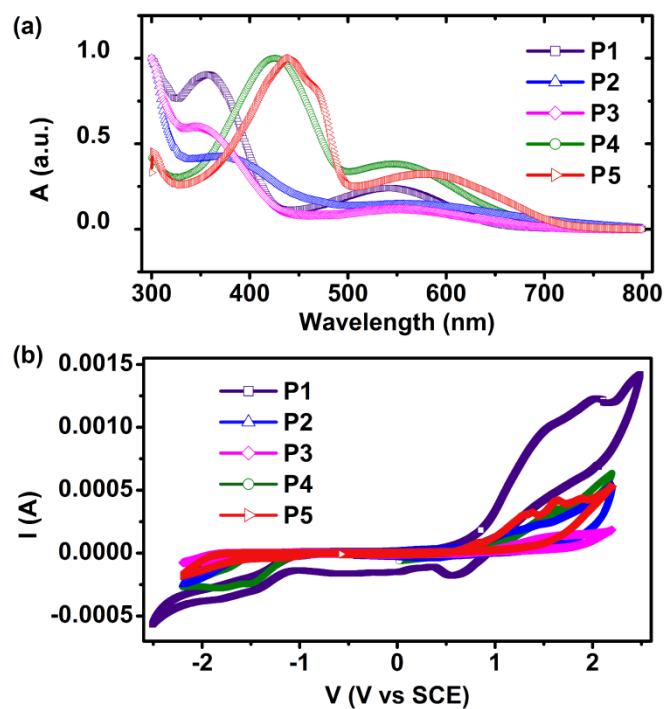


Figure 1. UV-vis spectra and cyclic voltammograms of **P1-P5**.

Au/Polymer/Pt memory devices have been fabricated and the schematic structure is depicted in Figure 2a. Herein, we use the *I-V* curves of Au/**P2**/Pt memory devices to describe memory effect of three water-soluble polymers. The resistance of the as-fabricated devices is $\sim 147\text{ K}\Omega$ and this initial device state can be defined as OFF state or high resistance state (HRS). During the *I-V* measurement, the bottom electrode (Pt) was grounded. The typical resistance switching process (current-voltage (*I-V*) characteristic) of Au/**P2**/Pt devices is shown in Figure 2b. By applying a positively-biased sweeping from 0 to 1.02 V (sweep 1, see Figure 2b), the current increases consecutively from $\sim 100\text{ nA}$ to $\sim 0.3\text{ mA}$. By further increasing the positive voltages, the current increase abruptly at $\sim 1.02\text{ V}$, indicating that the device switches from a HRS to a low resistance state (LRS or ON state), and this transition is defined as a “Write” or “SET” process. A current compliance (1 mA in this work) is usually needed during the “SET” process to prevent a permanent breakdown of the device. By sweeping the voltage from 1.02 to

2 V, and 2 to -0.48 V, the device holds on the LRS (sweeps 2 and 3), suggesting the non-volatile characteristic of this memory device. However, once the voltage exceeds -0.48 V, this device switches from LRS to HRS gradually, and this process is generally called “Erase” or “RESET” process. The

HRS can be maintained until next “Read” process (sweep 4). The above operations from sweep 1 to 4 are a rounded “Write-Read-Erase-Read” process. An ON/OFF ratio of ~ 500 is achieved at 0.1 V in this memory device, which is large enough to avoid misreading for peripheral circuits.

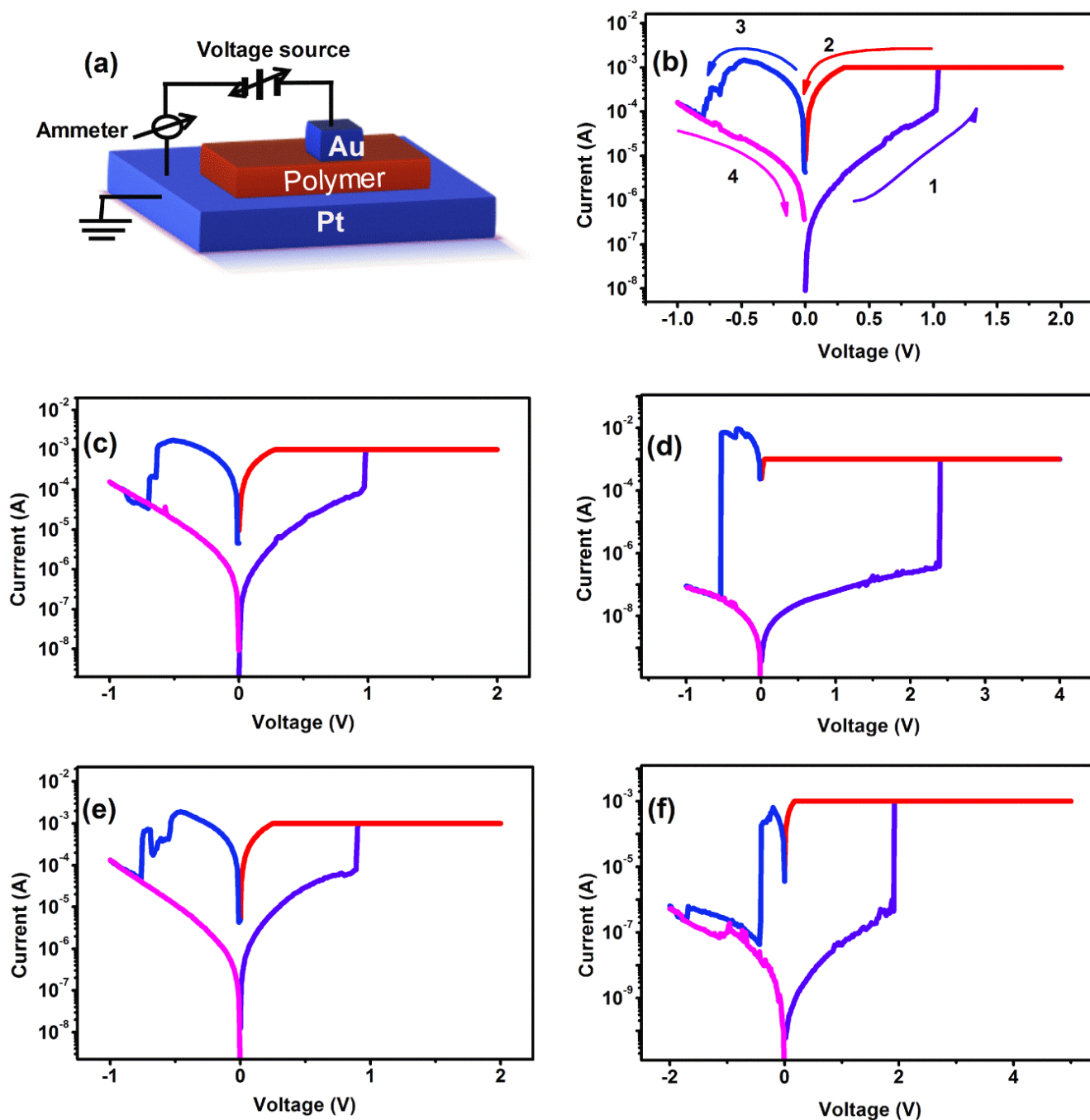


Figure 2. (a) Schematic illustration of the WSCPs-based ONVM devices; and the I–V cycles of the Au/Polymer/Pt devices based on (b) P2, (c) P3, (d) P1, (e) P5 and (f) P4. The sweep sequence of the applied voltage was shown in (b).

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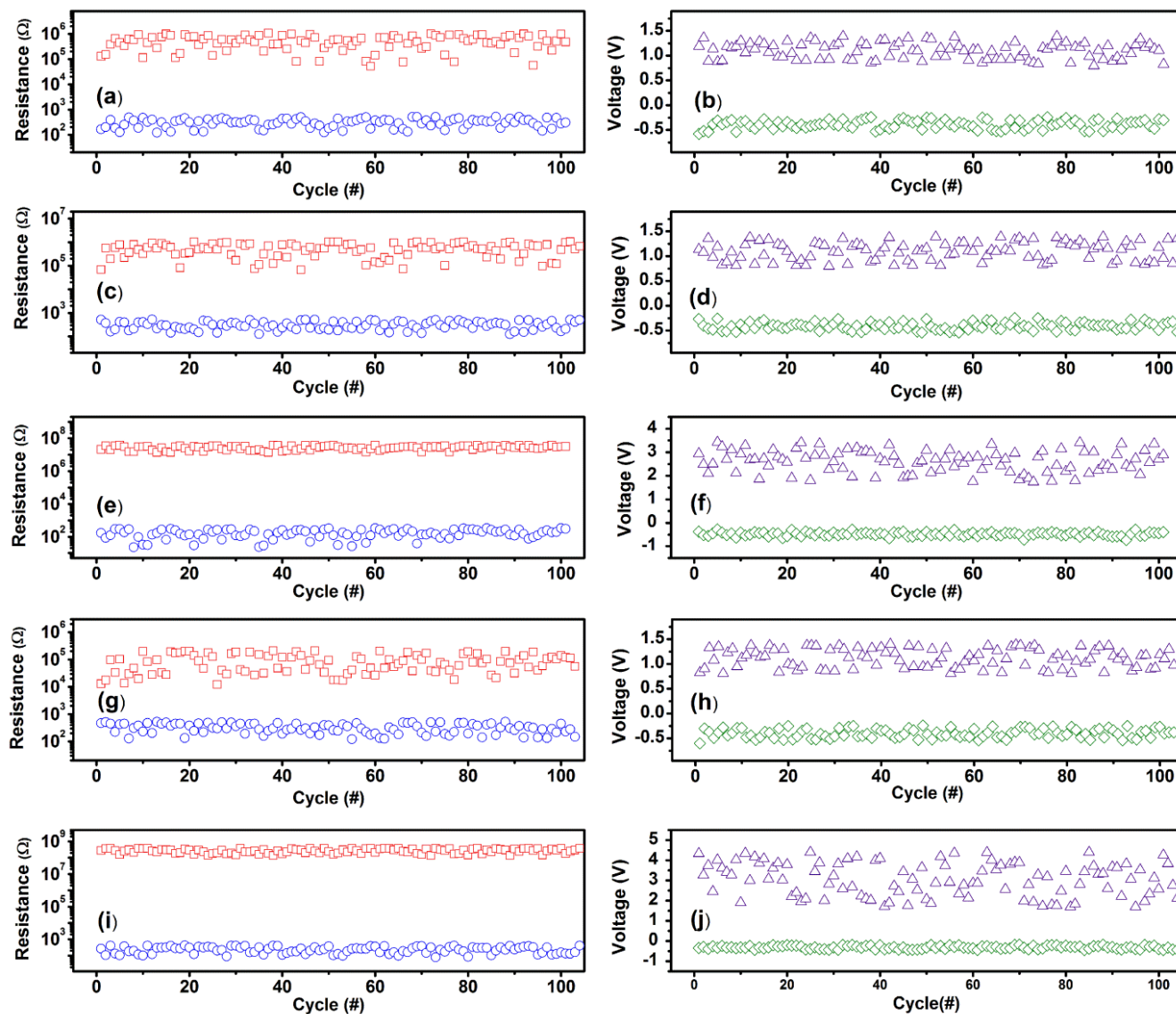


Figure 3. The endurance of the Au/Polymer/Pt devices. The resistance distribution of P2 (a), P3 (c), P1 (e), P5 (g) and P4 (i), and the switching voltage distribution of P2 (b), P3 (d), P1 (f), P5 (h) and P4 (j). The resistances of ON states and OFF state, the SET voltage, the RESET voltage are represented as red squares, blue cycles, purple triangles and olive diamonds, respectively.

The memory effects of WSCP **P3** and **P5** were also characterized by I-V curves (**Figure 2c** and **Figure 2e**). The two WSCPs-based devices show good memory performance. The SET voltage, RESET voltage and ON/OFF ratio of Au/P3/Pt devices are 0.97 V, -0.51 V and ~450, respectively. The SET voltage, RESET voltage and ON/OFF of Au/P5/Pt devices are 0.89 V, -0.46 V and ~228, respectively. Compared to WSCPs, the resistance switching of neutral polymers has the similar I-V curves except larger SET voltage and ON/OFF ratios, which are shown in **Figure 2d** and **Figure 2f**. These

differences will be discussed later in the switching mechanism part.

In order to investigate the endurance performance of the Au/polymer/Pt memory devices, cyclic switching operations are conducted. As shown in **Figure 3**, all five polymers exhibit good endurance (>100 cycles). The resistance values of **P1** and **P4** are read at -0.1 V, while the resistance values of **P2**, **P3** and **P5** are recorded at 0.1 V in each dc sweep. Although the resistances of the HRS and LRS scatter to a certain range, the

ON/OFF ratio of three WSCP **P2**, **P3**, and **P5** can keep ~ 100 and the cells didn't show obvious degradation after 100 cycles.

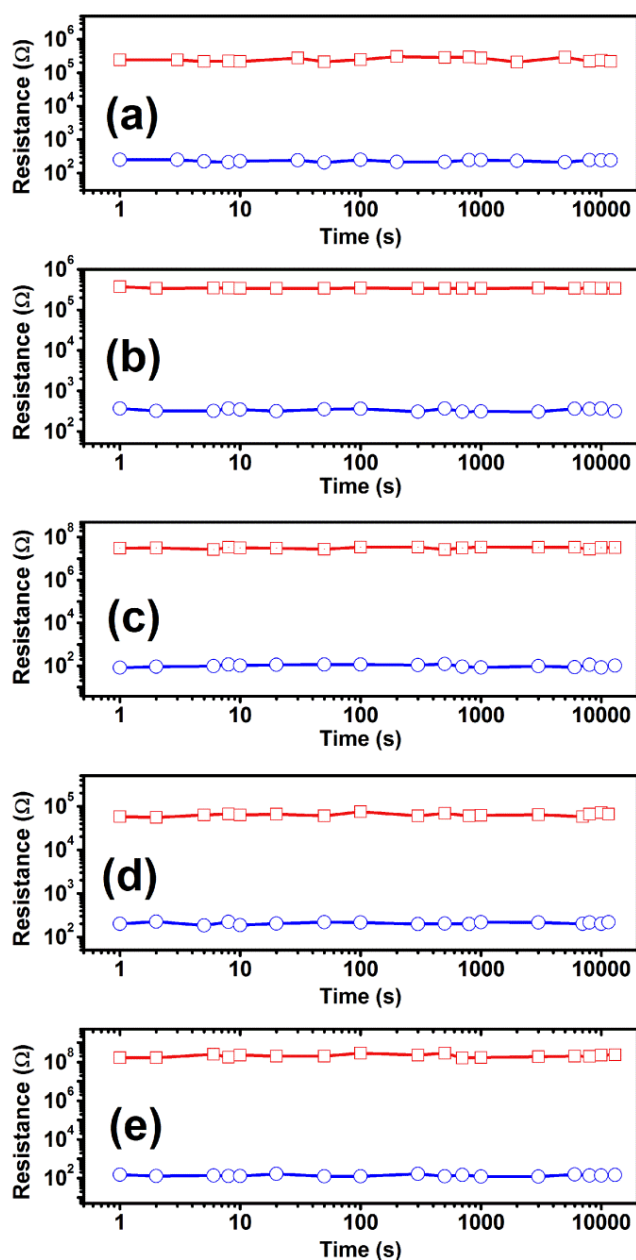


Figure 4. Retention of Au/Polymer/Pt devices based on P2 (a), P3 (b), P1 (c), P5 (d) and P4 (e). The resistances of ON and OFF states are represented as red squares and blue cycles, respectively.

The ON/OFF ratios of the neutral polymers **P1** and **P4** are more than 10^4 and the fluctuation of the ON/OFF ratios during the cyclic testing seems better than that of water-soluble polymers. Compared to the resistances of the ON and OFF states, the evolution of SET and RESET voltages of Au/Polymer/Pt memory devices shows large fluctuation. Especially the distribution of the SET and RESET voltages for two neutral polymers **P1** and **P4** shows a voltage range of more than 2.0 V, whereas the voltages of WSCPs are in a much narrow range (less than 1.0 V). The endurance measurement ensures that the resistance switching is controllable, reversible

and reproducible. **Figure 4** shows the retention of the memory cells at room temperature read at 0.1 V for **P2**, **P3** and **P5**, and -0.1 V for **P1** and **P4**. The readout is nondestructive. Both LRS and HRS states of devices based on **P1-P5** can be retained for more than 10^4 s without external electrical power supply, indicating that the memory devices is nonvolatile and stable at room temperature.

The mechanism of the resistive switching of the neutral and WSCP memory devices can be attributed to the charge transfer effect. In the chemical structures of these polymer backbones, fluorene/carbazole moieties are electron donors, while the benzothiadiazole units are electron acceptors. The I - V curves of SET processes for all five polymers were replotted in a log-log scale, shown in **Figure S4**. The Ohmic conduction model, which satisfactorily fits the respective I - V curves, is dominant in the ON states. However, the conduction mechanism of the HRS is more complicated. Curve-fitting results suggest that the HRS charge transport behaviour is in good agreement with a classical space charge limited current (SCLC), which consists of three portions: the Ohmic region ($I \propto V$), the Child's law region ($I \propto V^2$), and the steep current increase region ($I \propto V^n$, $n \geq 3$).^{3,19} Though the switching mechanisms of the devices based on all five polymers are possibly charge transfer between donors and acceptors, there are some noticeable differences in the switching process between neutral polymers and WSCPs. In OFF states, there are many ions in WSCPs (**P2**, **P3** and **P5**), so the current of the OFF states in the devices based on WSCPs are 2-3 order of magnitudes higher than those in neutral polymers. Similarly, more ions in WSCPs are more useful to form a conductive path in these devices than those in neutral polymers. As a result, the SET voltages in the devices based on water-soluble polymers are smaller than that in neutral polymers.

Conclusions

In summary, three water-soluble conjugated D-A polymers was synthesized and memory devices based on these WSCPs display good performance. In addition, different kinds of donors/acceptors and ion types have been employed in WSCPs to optimize the performance of ONVMs. More importantly, these devices are fabricated in an environmental-friendly way, in other words, a universal water-processable method to fabricate ONVMs has been developed. Our results could provide a green way to construct a new type of high performance ONVMs.

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Notes and references

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† Electronic Supplementary Information (ESI) available: the detail of synthesis and characterization, the ¹H NMR, FT-IR, TGA and the simulation of *I-V*. See DOI: 10.1039/b000000x/

1. a) Q.-D. Ling, F.-C. Chang, Y. Song, C.-X. Zhu, D.-J. Liaw, D. S.-H. Chan, E.-T. Kang, K.-G. Neoh, *J. Am. Chem. Soc.* 2006, **128**, 8732; b) J. H. Oh, H. W. Lee, S. Mannsfeld, R. M. Stoltenberg, E. Jung, Y. W. Jin, J. M. Kim, J.-B. Yoo, Z. Bao, *Proc. Natl. Acad. Sci.* 2009, **106**, 6065; c) T. Sekitani, H. Nakajima, H. Maeda, T. Fukushima, T. Aida, K. Hata, T. Someya, *Nat. Mater.* 2009, **8**, 494; d) Y. Li, P. Sonar, S. P. Singh, M. S. Soh, M. van Meurs, J. Tan, *J. Am. Chem. Soc.* 2011, **133**, 2198; e) G. Li, R. Zhu, Y. Yang, *Nat. Photon.* 2012, **6**, 153; f) I. Osaka, M. Shimawaki, H. Mori, I. Doi, E. Miyazaki, T. Koganezawa, K. Takimiya, *J. Am. Chem. Soc.* 2012, **134**, 3498.
2. a) R. J. Tseng, C. Tsai, L. Ma, J. Ouyang, C. S. Ozkan, Y. Yang, *Nat. Nano.* 2006, **1**, 72; b) G. Sonmez, H. Meng, Q. Zhang, F. Wudl, *Adv. Funct. Mater.* 2003, **13**, 726; c) J. Zhang, C. Wang, W. Chen, J. Wu, Q. Zhang, *RSC advances*, 2015, **5**, 25550.
3. a) Q.-D. Ling, D.-J. Liaw, C. Zhu, D. S.-H. Chan, E.-T. Kang, K.-G. Neoh, *Prog. Polym. Sci.* 2008, **33**, 917; b) J. Wu, Y. Sun, W.-B. Pei, L. Huang, W. Xu, Q. Zhang, *Syn Met.* 2014, **196**, 173-177; c) J. Wu, Y. Sun, W. Xu, Q. Zhang, *Syn Met.* 2014, **189**, 177.
4. a) L.-H. Xie, Q.-D. Ling, X.-Y. Hou, W. Huang, *J. Am. Chem. Soc.* 2008, **130**, 2120; b) S.-J. Liu, Z.-H. Lin, Q. Zhao, Y. Ma, H.-F. Shi, M.-D. Yi, Q.-D. Ling, Q.-L. Fan, C.-X. Zhu, E.-T. Kang, W. Huang, *Adv. Funct. Mater.* 2011, **21**, 979; c) S.-J. Liu, P. Wang, Q. Zhao, H.-Y. Yang, J. Wong, H.-B. Sun, X.-C. Dong, W.-P. Lin, W. Huang, *Adv. Mater.* 2012, **24**, 2901; d) X.-D. Zhuang, Y. Chen, G. Liu, P.-P. Li, C.-X. Zhu, E.-T. Kang, K.-G. Neoh, B. Zhang, J.-H. Zhu, Y.-X. Li, *Adv. Mater.* 2010, **22**, 1731; e) X.-D. Zhuang, Y. Chen, B.-X. Li, D.-G. Ma, B. Zhang, Y. Li, *Chem. Mater.* 2010, **22**, 4455.
5. a) 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; b) B. Zhang, G. Liu, Y. Chen, C. Wang, K.-G. Neoh, T. Bai, E.-T. Kang, *ChemPlusChem* 2012, **77**, 74; c) G. Liu, X. Zhuang, Y. Chen, B. Zhang, J. Zhu, C.-X. Zhu, K.-G. Neoh, E.-T. Kang, *Appl. Phys. Lett.* 2009, **95**, 253301; d) G. Liu, B. Zhang, Y. Chen, C.-X. Zhu, L. Zeng, D. Siu-Hung Chan, K.-G. Neoh, J. Chen, E.-T. Kang, *J. Mater. Chem.* 2011, **21**, 6027.
6. a) J. Xiao, Z. Yin, H. Li, Q. Zhang, F. Boey, H. Zhang, Q. C. Zhang, *J. Am. Chem. Soc.* 2010, **132**, 6926; b) J. Xiao, Z. Yin, Y. Wu, J. Guo, Y. Cheng, H. Li, Y.-Z. Huang, Q. Zhang, J. Ma, F. Boey, H. Zhang, Q.-C. Zhang, *Small*, 2011, **7**, 1242; c) G. Li, K. Zheng, C. Wang, K. S. Leck, F. Hu, X. W. Sun, Q. Zhang, *ACS Applied Mater. Interface* 2013, **5**, 6458; d) P.-Y. Gu, J. Gao, C.-J. Lu, C. Wang, G. Li, F. Zhou, Q.-F. Xu, J.-M. Lu, Q. Zhang, *Materials Horizons*, 2014, **1**, 446; e) C. Wang, J. Wang, P. Li, J. Gao, S. Y. Tan, W. Xiong, B. Hu, P. S. Lee, Y. Zhao, Q. Zhang, *Chem Asian J.* 2014, **9**, 779; f) C. Wang, B. Hu, J. Wang, J. Gao, G. Li, W.-W. Xiong, B. Zou, M. Suzuki, N. Aratani, H. Yamada, F. Huo, P. S. Lee, Q. Zhang, *Chem. Asian J.* 2015, **10**, 116.
7. a) 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; b) K. Asadi, M. Li, N. Stingelin, P. W. M. Blom, D. M. de Leeuw, *Appl. Phys. Lett.* 2010, **97**, 193308.
8. 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.
9. a) B. Hu, F. Zhuge, X. Zhu, S. Peng, X. Chen, L. Pan, Q. Yan, R.-W. Li, *J. Mater. Chem.* 2012, **22**, 520; b) 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; c) B. Hu, R. Quhe, C. Chen, F. Zhuge, X. Zhu, S. Peng, X. Chen, L. Pan, Y. Wu, W. Zheng, Q. Yan, J. Lu, R.-W. Li, *J. Mater. Chem.* 2012, **22**, 16422.
10. a) J. Kim, B. A. Grzybowski, *Adv. Mater.* 2012, **24**, 1850; b) S. Nau, S. Sax, E. J. W. List-Kratochvil, *Adv. Mater.* 2014, **26**, 2508; c) R. J. Tseng, C. O. Baker, B. Shedd, J. Huang, R. B. Kaner, J. Ouyang, Y. Yang, *Appl. Phys. Lett.* 2007, **90**, 053101; d) A. Bandyopadhyay, S. Sahu, M. Higuchi, *J. Am. Chem. Soc.* 2011, **133**, 1168; e) B. Lei, W. L. Kwan, Y. Shao, Y. Yang, *Org. Electron.* 2009, **10**, 1048; f) Y. Li, A. Sinitskii, J. M. Tour, *Nat. Mater.* 2008, **7**, 966.
11. B. Cho, J.-M. Yum, S. Song, Y. Ji, D.-Y. Kim, T. Lee, *Adv. Funct. Mater.* 2011, **21**, 3976.
12. a) B. Cho, S. Song, Y. Ji, T.-W. Kim, T. Lee, *Adv. Funct. Mater.* 2011, **21**, 2806; b) S.-T. Han, Y. Zhou, V. A. L. Roy, *Adv. Mater.* 2013, **25**, 5425; c) P. Heremans, G. H. Gelinck, R. Müller, K.-J. Baeg, D.-Y. Kim, Y.-Y. Noh, *Chem. Mater.* 2011, **23**, 341; d) G. Jiang, Y. Song, X. Guo, D. Zhang, D. Zhu, *Adv. Mater.* 2008, **20**, 2888; e) Y. Yang, J. Ouyang, L. Ma, R. J.-H. Tseng, C.-W. Chu, *Adv. Funct. Mater.* 2006, **16**, 1001.
13. a) P. M. Beaujuge, C. M. Amb, J. R. Reynolds, *Adv. Mater.* 2010, **22**, 5383; b) C. Duan, K. Zhang, X. Guan, C. Zhong, H. Xie, F. Huang, J. Chen, J. Peng, Y. Cao, *Chem. Sci.* 2013, **4**, 1298; c) F. Huang, L. Hou, H. Wu, X. Wang, H. Shen, W. Cao, W. Yang, Y. Cao, *J. Am. Chem. Soc.* 2004, **126**, 9845; d) B. Liu, G. C. Bazan, *J. Am. Chem. Soc.* 2006, **128**, 1188.
14. a) C. Duan, W. Cai, B. B. Y. Hsu, C. Zhong, K. Zhang, C. Liu, Z. Hu, F. Huang, G. C. Bazan, A. J. Heeger, Y. Cao, *Energy Environ. Sci.* 2013, **6**, 3022; b) J. Fang, B. H. Wallikewitz, F. Gao, G. Tu, C. Müller, G. Pace, R. H. Friend, W. T. S. Huck, *J. Am. Chem. Soc.* 2010, **133**, 683; c) Y. H. Zhou, C. Fuentes-Hernandez, J. Shim, J. Meyer, A. J. Giordano, H. Li, P. Winget, T. Papadopoulos, H. Cheun, J. Kim, M. Fenoll, A. Dindar, W. Haske, E. Najafabadi, T. M. Khan, H. Sojoudi, S. Barlow, S. Graham, J.-L. Bredas, S. R. Marder, A. Kahn, B. Kippelen, *Science*, 2012, **336**, 327.
15. a) A. Duarte, K.-Y. Pu, B. Liu, G. C. Bazan, *Chem. Mater.* 2010, **23**, 501; b) F. Huang, H. Wu, Y. Cao, *Chem. Soc. Rev.* 2010, **39**, 2500.
16. R.-H. Lee, J.-K. Liu, J.-H. Ho, J.-W. Chang, B.-T. Liu, H.-J. Wang, R.-J. Jeng, *Polym. Inter.* 2011, **60**, 483.
17. B. Bao, L. Yuwen, X. Zhan, L. Wang, *J. Polym. Sci. Part A Polym. Chem.* 2010, **48**, 3431.
18. A. Balamurugan, M. L. P. Reddy, M. Jayakannan, *J. Polym. Sci. Part A Polym. Chem.* 2009, **47**, 5144.
19. S. M. Sze, K. K. Ng. *Physics of Semiconductor Devices*. 3rd ed. Wiley, Hoboken, NJ, USA 2007.