Flexible Memory Devices with Tunable Electrical Bistability via Controlled Energetic in Donor-Donor and Donor-Acceptor Conjugated Polymers

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GRAPHIC ABSTRACT

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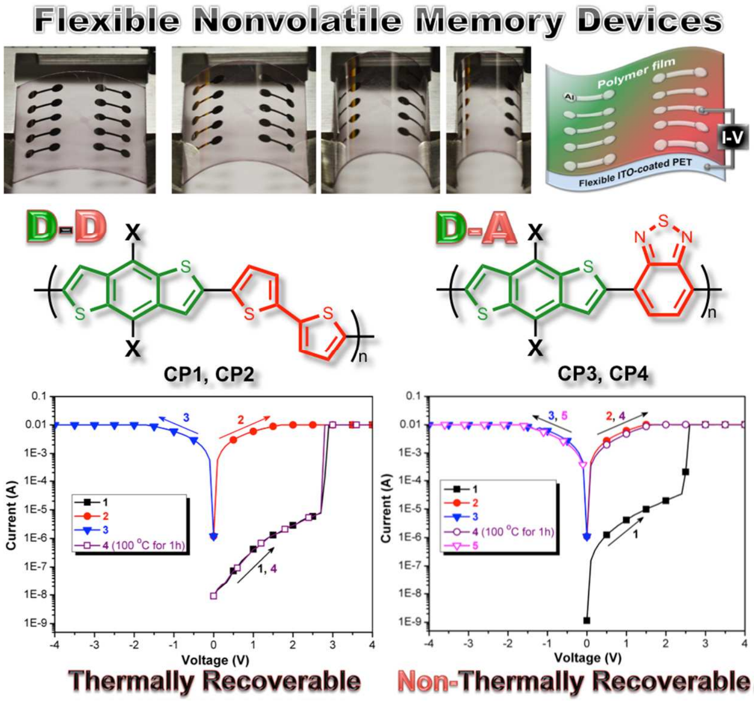
Hung-Ju Yen, Hsinhan Tsai, Cheng-Yu Kuo, Wanyi Nie, Aditya D. Mohite, Gautam Gupta, Jian Wang, Jia-Hao Wu, Guey-Sheng Liou and Hsing-Lin Wang*

Flexible nonvolatile memory devices were fabricated from benzodithiophene-based donor-donor and donor-acceptor 2D conjugated polymers with thermally/non-thermally recoverable memory behaviors.



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Flexible nonvolatile memory devices were fabricated from benzodithiophene-based donor-donor and donor-acceptor conjugated polymers with thermally/non-thermally recoverable memory behaviors.

In recent years, the application of conjugated materials in optoelectronic devices such as light-emitting diodes,[1] solar cells,[2] thin film transistors,[3] electrochromic,[4] and memory devices[5] have attracted tremendous attention, due to their rich structural flexibility, low-cost, solution processability, large area fabrication, and three-dimensional stacking capability.[6] The emerging research for information storage in the form of high (ON) and low (OFF) current state in place of the amount of charges stored in silicon devices is to improve and/or enhance the superiority of higher data storage density, ease of miniaturization, longer data retention time, faster speed, lower power consumption, and cost-effective processing for practical use.[7] Polymeric materials with electrical bistability resulting from different electronic structure in response to the applied electric field begin to stand out conspicuously and have predominance in scaling down from micro-scale to nano-scale for memory device. Thus, polymeric memory devices have been developed as a promising alternative to the conventional semiconductor-based memory devices.

In the initial stage of memory devices, polymers were used as polyelectrolytes and matrices.[8] Recently, design synthesis of polymers with specific structures that can provide desired electronic properties is a holy grail in developing efficient polymeric memory devices. For resistive type memory materials, several models of different mechanisms that can lead to electrical memory behaviours have been illustrated such as charge transfer (CT), conductive filament formation, and charge trapping/de-trapping.[5a] A few precedents using donor-acceptor systems have been demonstrated, including conjugated polymers (CPs),[9] non-conjugated polymers with donor/acceptor chromophores,[5b, 5d] and polymer nanocomposites.[10]

Among all donor-acceptor systems studied, CPs have been utilized to fabricate different types of memories, such as volatile dynamic random access memory (DRAM), static random access memory (SRAM), and nonvolatile write-once-read-many-times (WORM). The electronic memory behaviors were found to be highly dependent on molecular structure of the materials, which dictates properties such as the occurrence of charge transfer, turn on voltage, and charge trapping.[5a] As nonvolatile memory that is capable of holding data permanently and being read repeatedly, WORM memory and flash-type memory are very desirable for ultralow-cost permanent storage of digital images because of eliminating the need for slow, bulky, and expensive mechanical drives used in conventional magnetic and optical memories.[7] Basically, the WORM memory functions as conventional CD-R, DVD-R, or programmable read-only memories (PROMs) can also be used as disposable memories in some niche areas, such as electronic labels and radio-frequency identification (RFID) tags.

Benzodithiophene (BDT)-based CPs have garnered considerable interest in the past few years due to their good performance in both organic field-effect transistors and solar cells.[11] In addition to the planar backbone, attaching different substituents to BDT core offers the flexibility of fine-tune the energy levels of the resulting polymers. The electronic structure could be easily modulated by adjusting structure and affinity of the donor[2b] and/or acceptor moieties.[2c] Moreover, the emerged BDT-based two-dimensional CPs with alkylthienyl side chains could effectively increase the structure order, enhance processability, offer broader absorption spectra, and lower the HOMO energy levels, hence, improve the photovoltaic properties of the device.[2a]

In this communication, *we report for the first time thienyl BDT-based conjugated polymeric flexible memory devices with thermally recoverable WORM behaviors.* A series of two-dimensional BDT-based CPs **CP1-CP4** with terthienyl/bithienyl side chains[12] were employed for memory device applications (Figure 1a and 1b). The incorporation of terthienyl and bithienyl side chains allows the attachment of up to eight and six alkyl substituents per BDT repeating unit, respectively, which in turn produces organosoluble CPs with ease of processability, high molecular weight and improved film quality. Moreover, the electron-abundant bithiophene and electron-deficient benzothiadiazole units were chosen as part of the polymer backbone to construct donor-donor and donor-acceptor conjugated backbone systems.

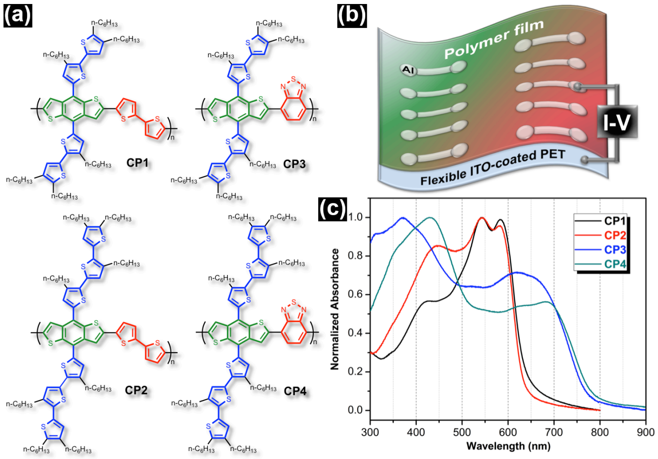

Figure 1. (a) Chemical structures of CPs, (b) configuration of the flexible memory device, and (c) normalized absorption spectra of polymer thin films.

The UV-vis absorption spectrum of **CP1**-**CP4** is depicted in Figure 1c and the optical energy band gap (E_g) is estimated by the onset wavelength. The smaller band gap energy of the benzothiadiazole-based polymers **CP3** and **CP4** (~1.60 eV) as oppose to bithiophene-based polymers **CP1** and **CP2** (~1.95 eV) is mainly due to the electron-deficient acceptor benzothiadiazole unit. Benzothiadiazole coupled with electron-rich BDT core gives rise to a charge transfer characteristic accompanied by increasing persistent length of the polymer backbone and samller band gap energy.

The electrochemical properties of these polymers were investigated by cyclic voltammetry (CV, Figure S1). All the polymers exhibit clear oxidation and reduction couples at the onset potential (E_{onset}) of around 0.97 to 1.05 V and -0.91 to -1.27 V, respectively. The redox potentials of the polymers and their respective HOMO and LUMO (versus vacuum) are calculated and summarized in Table S1. The similar HOMO levels for all polymers implying that the HOMO is basically localized on the donor BDT cores. In addition, the LUMO levels of the benzothiadiazole-based donor-acceptor polymers **CP3** and **CP4** are around -3.50 eV, which is 0.30 eV lower than the LUMO of bithiophene-based donor-donor polymers **CP1** and **CP2**. The results suggest that the introduction of electron-deficient unit can effectively increase the electron affinity of benzothiadiazole-based polymers and lower LUMO levels.

The memory behaviors of these polymers were depicted by the current-voltage (*I*-*V*) curves on an ITO-coated PET (polyethylene terephthalate)/polymer CPs/Al sandwich device as shown in Figure 2 and 3. Within the flexible device, CP films were used as an active layer with Al and ITO as the top and bottom electrodes, respectively (Figure 1b). Polymer film thickness was optimized around 160 nm and was used for all devices. Figure 2 exhibits the *I*-*V* curve of donor-donor polymers **CP1** and **CP2**, which was measured with a compliance current of 0.01 A. Initially, the current of the as-fabricated device is low (defined as the OFF state). During the first negative sweep from 0 V to -4 V (Figure 2a and 2c), the current increased gradually from 10^{-7} to 10^{-5} in bias ranged 0 to -3 V followed by a rapid increase to 10^{-2} A corresponding to the threshold voltage of around -3.0 V, indicating the transition from the OFF state to a high-conductivity (ON) state with an ON/OFF current ratio of 10^3 to 10^5. In a memory device, this OFF-to-ON transition can be defined as a "writing" process. The device remained in the ON state during the subsequent negative scan (the second sweep) and then positive scan (the third sweep). The memory device can not be reset to the initial OFF state by applying a reverse electric field implying the non-erasable behavior. In addition, the ON state could also remain once the memory devices have been switched to the ON state at around 3.0 V (Figure 2b and 2d), even after turn off power for an extended period of time (greater than a few hours). These results indicate that **CP1** and **CP2** films both exhibit nonvolatile WORM memory behaviors.

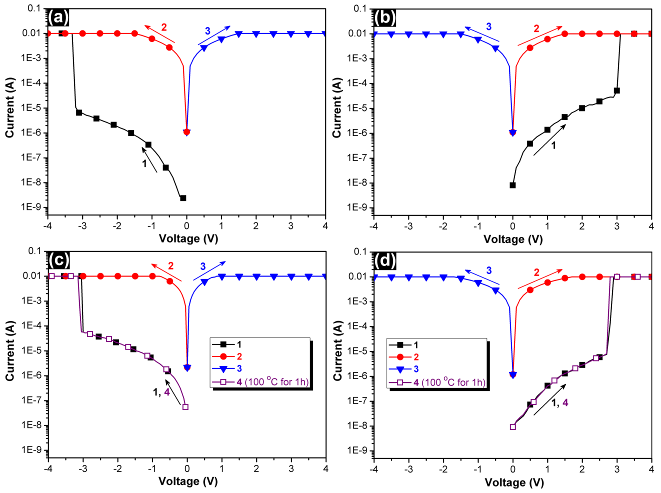

Figure 2. Current-voltage (*I*-*V*) characteristics of the ITO/CPs (160±10 nm)/Al memory device for donor-donor CPs with the first sweep performed negatively: (a) **CP1**, (c) **CP2** and positively: (b) **CP1**, (d) **CP2**.

I-*V* curves of donor-acceptor polymers **CP3** and **CP4** are summarized in Figure 3, revealing nonvolatile WORM behaviors with the lower threshold voltages around -2.0 and 2.5 V for negative and positive sweeps, respectively. The slightly lower threshold voltages of **CP3** and **CP4** as oppose to **CP1** and **CP2** could be attributed to the donor-acceptor ability, which originates from the intra-chain charge transfer character. On the other hand, the turn on voltage of terthienyl-substituted polymers is 0.1-0.2 V lower than bithiophene-substituted polymers presumably due to their extended conjugation. This suggests strong correlation between molecular structure and memory device properties. Threshold voltage, current and reversibility of the devices can be tailored through control synthesis of conjugated polymers with backbone and side chains allowing fine-tuning the energetics and degree of conjugation.

Taking into consideration of the memory characteristics, we fabricated and investigated **CP4**–based memory devices with various thicknesses (Figure S2). We found that device with 120 nm thick **CP4** film always exhibits high conductivity in positive and negative voltage sweeps. As observed for the 120 nm thick films, the 160 and 200 nm thick films both exhibit WORM memory characteristics in positive and negative voltage sweeps. The results also suggest that the devices with thinner films have lower switching threshold voltages. Furthermore, the devices with thickness higher than 240 nm only exhibit low conductivity in positive/negative sweeps and have no electrical switching behavior.[5d, 13]

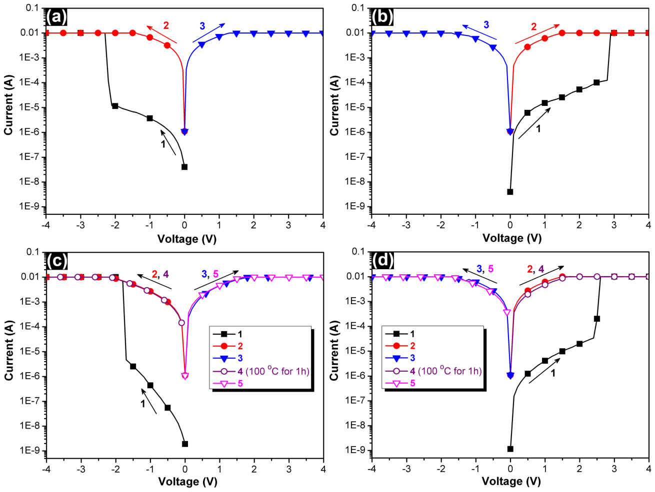

Figure 3. Current-voltage (*I-V*) characteristics of the ITO/CPs (160±10 nm)/Al memory device for donor-acceptor CPs with the first sweep performed negatively: (a) **CP3**, (c) **CP4** and positively: (b) **CP3**, (d) **CP4**.

In order to demonstrate the feasibility of the switching property of flexible device, the device based on **CP1** was physically fixing to a vernier caliper from flat to bent conditions (Figure 4a). The memory device was tested under severe bending at various radii of curvature, 11, 9, 7, and 5 mm, respectively, and the device remains intact. We also measured the switching memory behavior of the device under mechanical bending stress. Our results show reliable and reproducible memory properties under bending stress (Figure 4b); throughout the bending process, we observe basically identical threshold voltage and similar current. Bending reveals no impact on change in polymer chain conformations and electronic properties, which are two very important qualities for retaining stability of flexible devices.

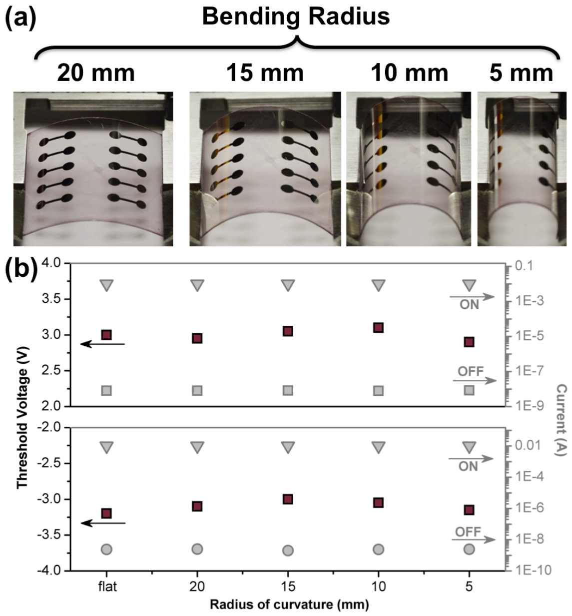

Figure 4. (a) Appearance in various bent states and (b) variation of current and threshold voltage with different bending radius of the ITO/**CP1**/Al flexible memory device.

The molecular geometry and electronic structures of the polymers can help better understand the electronic process occurring inside the thin films. For gaining valuable insight to the memory behaviors of the polymeric devices, we calculated the molecular orbital and electric density contours of the basic units by molecular simulation. The molecular simulation on the basic unit of CPs was carried out by DFT/B3LYP/6-31G(d) with the Gaussian 09 program. The charge density isosurfaces of the basic unit, the most energetically favorable geometry, HOMO and LUMO energy levels of CPs are depicted in Figure 5a. The mechanism of electronic transition of CPs can be explained from the electric field induced CT effect between the donor and acceptor. The excitation of the donor units leads to the intra- or intermolecular CT states. With the interaction between donor and acceptor, CT process gives rise to a charge separated and conductive state. For donor-acceptor polymers **CP3** and **CP4**, it is obvious that benzothiadiazole unit contributes more to the LUMO while thienyl-BDT contributes more to the HOMO. Therefore, the memory devices based on **CP3** and **CP4** both exhibit very stable ON states once the devices were written since the high electron-accepting ability of the benzothiadiazole unit can stabilize the formed CT complex.

On the other hand, the HOMO energy levels of polymers **CP1** and **CP2** were distributed at the electron-donating thienyl-substituted BDT moieties along with bithiophene backbone, indicating that the electron pull–push effect in donor-donor CPs is not obvious. Upon undergoing transition from HOMO to LUMO, only a slight transition of the electron density from the terthienyl/bithienyl side chains to BDT-bithiophene backbone occurred. This transition would be easily recovered under a reverse voltage or even automatically revert to the OFF state, leading to the Flash or DRAM memory behavior. However, since the LUMO energy level is a dominant factor for memory behavior, the electron could locate on the electron acceptor side (BDT-bithiophene), a new stable charge-separated state, and thus showed the WORM characteristics. It is important to note that there is a possibility to reverse the electron transfer process with external stimuli because bithiophene is not a strong acceptor.[14] Consequently, we carried out comparative studies of thermal stability between **CP2** and **CP4** with WORM memory behaviors, the results were summarized in Figure 2c, 2d, 3c, and 3d. After heating at 100 °C for 1 hour, the ON state of **CP2** recovered to the original OFF state due to a weaker charge-separated state. On the contrary, the **CP4**-based memory device maintained its high conductivity after thermal treatment. These results are consistent with the proposed mechanism derived from molecular simulation and offer a design concept for thermally/non-thermally recoverable WORM memory devices, revealing great promises for advanced memory devices.

Based on our proposed mechanism, the energy diagram of CPs and the work function of the electrodes is shown in Figure 5. When the positive sweep was conducted, the hole was easily injected from the top electrode Al to the HOMO of polymer with an energy barrier of 1.2 eV between Al (-4.2 eV) and HOMO (~-5.4 eV) as shown in Figure 5b. On the contrary, during negative sweep, hole is easier to be injected from bottom electrode ITO into HOMO of the polymer because of smaller energy barrier (0.6 eV) between the work function of ITO (-4.8 eV) and HOMO of the polymers (~-5.4 eV), thus the memory device can be switched to the ON state at lower threshold voltages as oppose to the positive sweep (Figure 5c). We use ease/easier to describe the property of memory devices and magnitude of the energy barrier between energy levels of polymers and metal work functions. The so-called "hard" is typically refer to the devices that cannot be switched to the ON state. In addition, the donor-acceptor polymers **CP3** and **CP4** with lower LUMO energy levels can be switched to ON state at lower threshold voltages in positive/negative sweeps due to smaller energy barrier between LUMO (~-3.5 eV) and work function of ITO/Al as oppose to the donor-donor ones with higher LUMO levels (~-3.2 eV). For **CP1** and **CP2**, the symmetrical *I-V* curves for positive and negative sweep have comparable threshold voltages can be explained as the electrical switching arises from the electric field-induced charge transfer rather than the hole injection process.[15] To further investigate the electrical switching characteristics of the memory devices, we analyzed the *I–V* characteristics of the OFF and ON states. The trap-limited space-charge limited conduction (SCLC) model was found to satisfactorily fit the *I–V* data for the OFF-state (Figure S3), while the Ohmic contact model was found to satisfactorily fit the *I–V* data for the ON-state (inset in Figure S3). This result indicates that a trap-limited SCLC mechanism is dominant in the OFF state and Ohmic conduction is dominant when the device is in the ON-state.[5d]

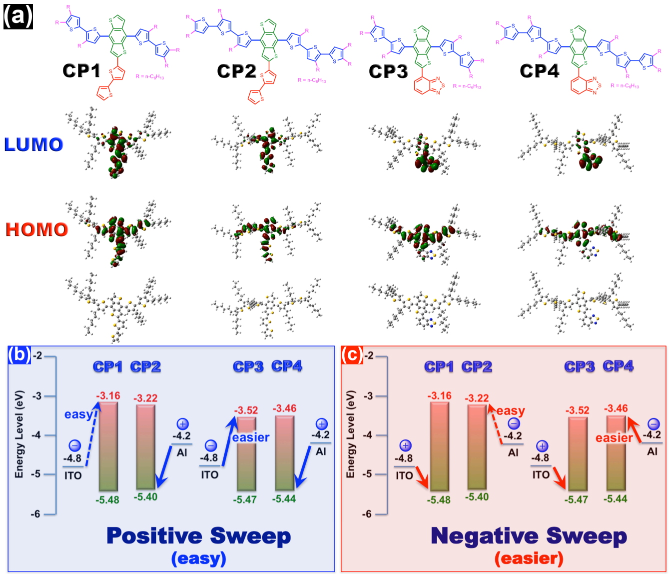

Figure 5. (a) Calculated molecular orbitals and corresponding energy levels of the basic units (BU) for CPs. HOMO and LUMO energy levels of CPs along with the work function of the electrodes for (b) positive sweep and (c) negative sweep.

In summary, we have achieved fabrication and characterization of thermal recoverable flexible nonvolatile memory devices based on 2-D conjugated polymers. Combined theoretical and experimental studies of our donor-acceptor and donor-donor conjugated systems offer valuable insights to improve memory devices by rational design of molecular structures. We have demonstrated a strong correlation between resistive switching properties and molecular structural through controlling the stability of CT complex. Our results suggest the feasibility of tailoring the memory device properties through control synthesis of conjugated polymers with backbone and side chains allowing fine-tuning the energetics and degree of conjugation. The novel thienyl BDT-based memory devices are flexible, thermally reversible, and have great promises for advanced organic electronics.

Notes and references

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1. (a) Q. B. Pei, G. Yu, C. Zhang, Y. Yang and A. J. Heeger, *Science*, 1995, **269**, 1086-1088; (b) R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlund and W. R. Salaneck, *Nature*, 1999, **397**, 121-128.
2. (a) L. J. Huo, J. H. Hou, S. Q. Zhang, H. Y. Chen and Y. Yang, *Angew. Chem. Int. Edit.*, 2010, **49**, 1500-1503; (b) D. Lee, E. Hubijar, G. J. D. Kalaw and J. P. Ferraris, *Chem. Mater.*, 2012, **24**, 2534-2540; (c) H. H. Cho, T. E. Kang, K. H. Kim, H. Kang, H. J. Kim and B. J. Kim, *Macromolecules*, 2012, **45**, 6415-6423.
3. (a) J. Rivnay, L. H. Jimison, J. E. Northrup, M. F. Toney, R. Noriega, S. F. Lu, T. J. Marks, A. Facchetti and A. Salleo, *Nat. Mater.*, 2009, **8**, 952-958; (b) H. Yan, Z. H. Chen, Y. Zheng, C. Newman, J. R. Quinn, F. Dotz, M. Kastler and A. Facchetti, *Nature*, 2009, **457**, 679-686.
4. (a) H. J. Yen and G. S. Liou, *Polym. Chem.*, 2012, **3**, 255-264; (b) H.-J. Yen, C.-J. Chen and G.-S. Liou, *Adv. Funct. Mater.*, 2013, **23**, 5307-5316.
5. (a) Q. D. Ling, D. J. Liaw, C. X. Zhu, D. S. H. Chan, E. T. Kang and K. G. Neoh, *Prog. Polym. Sci.*, 2008, **33**, 917-978; (b) S. J. Liu, P. Wang, Q. Zhao, H. Y. Yang, J. Wong, H. B. Sun, X. C. Dong, W. P. Lin and W. Huang, *Adv. Mater.*, 2012, **24**, 2901-2905; (c) S. G. Hahm, Y.-G. Ko, W. Kwon and M. Ree, *Current Opinion in Chemical Engineering*, 2013, **2**, 79-87; (d) K. Kim, Y.-K. Fang, W. Kwon, S. Pyo, W.-C. Chen and M. Ree, *J Mater Chem C*, 2013, **1**, 4858-4868.
6. A. Stikeman, *Technol. Rev.*, 2002, **105**, 31.
7. S. Moller, C. Perlov, W. Jackson, C. Taussig and S. R. Forrest, *Nature*, 2003, **426**, 166-169.
8. T. W. Kim, D. F. Zeigler, O. Acton, H. L. Yip, H. Ma and A. K. Y. Jen, *Adv. Mater.*, 2012, **24**, 828-833.
9. (a) H. C. Wu, A. D. Yu, W. Y. Lee, C. L. Liu and W. C. Chen, *Chem. Commun.*, 2012, **48**, 9135-9137; (b) H.-W. Lin, W.-Y. Lee, C. Lu, C.-J. Lin, H.-C. Wu, Y.-W. Lin, B. Ahn, Y. Rho, M. Ree and W.-C. Chen, *Polym. Chem.*, 2012, **3**, 767-777.
10. (a) X. D. Zhuang, Y. Chen, G. Liu, P. P. Li, C. X. Zhu, E. T. Kang, K. G. Neoh, B. Zhang, J. H. Zhu and Y. X. Li, *Adv. Mater.*, 2010, **22**, 1731-1735; (b) S. G. Hahm, N.-G. Kang, W. Kwon, K. Kim, Y.-G. Ko, S. Ahn, B.-G. Kang, T. Chang, J.-S. Lee and M. Ree, *Adv. Mater.*, 2012, **24**, 1062-1066.
11. I. F. Perepichka and D. F. Perepichka, in *Handbook of Thiophene-Based Materials*, John Wiley & Sons, Ltd, 2009.
12. C.-Y. Kuo, W. Nie, H. Tsai, H.-J. Yen, A. D. Mohite, G. Gupta, A. M. Dattelbaum, D. J. William, K. C. Cha, Y. Yang, L. Wang and H.-L. Wang, *Macromolecules*, 2014, **47**, 1008-1020
13. T. J. Lee, C.-W. Chang, S. G. Hahm, K. Kim, S. Park, D. M. Kim, J. Kim, W.-S. Kwon, G.-S. Liou and M. Ree, *Nanotechnology*, 2009, **20**, 135204.
14. (a) C.-J. Chen, H.-J. Yen, Y.-C. Hu and G.-S. Liou, *J Mater Chem C*, 2013, **1**, 7623; (b) G.-S. Liou, C.-J. Chen and J.-H. Wu, *Chem. Commun.*, 2014, DOI: 10.1039/C1033CC48569B.
15. (a) Y.-L. Liu, Q.-D. Ling, E.-T. Kang, K.-G. Neoh, D.-J. Liaw, K.-L. Wang, W.-T. Liou, C.-X. Zhu and D. S.-H. Chan, *J Appl Phys*, 2009, **105**, -; (b) Y.-Q. Li, R.-C. Fang, A.-M. Zheng, Y.-Y. Chu, X. Tao, H.-H. Xu, S.-J. Ding and Y.-Z. Shen, *J. Mater. Chem.*, 2011, **21**, 15643-15654.