Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Organic Donor-σ-Acceptor Molecules Based on 5,5′-(9,10-Bis((4-hexylphenyl)ethynyl)anthracene-2,6-diyl)bis(ethyne-2,1-diyl)bis(2-hexylthiophene) for Resistive Random Access Memory

Tae Wan Lee [a], Jicheol Shin [a], Kyung Hwan Kim [a], Min Ju Cho [a] & Dong Hoon Choi [a]

[a] Department of Chemistry, Research Institute for Natural Sciences, Korea University, Seoul, South Korea

Published online: 11 Sep 2013.

To cite this article: Tae Wan Lee, Jicheol Shin, Kyung Hwan Kim, Min Ju Cho & Dong Hoon Choi (2013) Organic Donor-σ-Acceptor Molecules Based on 5,5′-(9,10-Bis((4-hexylphenyl)ethynyl)anthracene-2,6-diyl)bis(ethyne-2,1-diyl)bis(2-hexylthiophene) for Resistive Random Access Memory, Molecular Crystals and Liquid Crystals, 580:1, 95-102, DOI: 10.1080/15421406.2013.807723

To link to this article: http://dx.doi.org/10.1080/15421406.2013.807723

Mol. Cryst. Liq. Cryst., Vol. 580: pp. 95–102, 2013

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.807723

Taylor & Francis
Taylor & Francis Group

Organic Donor-σ-Acceptor Molecules Based on 5,5′-(9,10-Bis((4-hexylphenyl)ethynyl)anthracene-2,6-diyl)bis(ethyne-2,1-diyl)bis(2-hexylthiophene) for Resistive Random Access Memory

TAE WAN LEE, JICHEOL SHIN, KYUNG HWAN KIM, MIN JU CHO, AND DONG HOON CHOI*

Department of Chemistry, Research Institute for Natural Sciences, Korea University, Seoul, South Korea

New Donor-σ-acceptor (D-σ-A) molecules of (HAT)-2(PDI) and (HAT)-2(PCBM); PDI refers to perylene diimide, PCBM refers to [6,6]-phenyl C61-butyric acid methyl ester, and HAT refers to 5,5′-(9,10-bis((4-hexylphenyl)ethynyl)anthracene-2,6-diyl)bis(ethyne-2,1-diyl)bis(2-hexylthiophene) were successfully synthesized for studying the intermolecular association behavior and their possible applications of these molecules to electrically bistable devices. The memory devices with the configuration of Al/(HAT)-2(PDI) or (HAT)-2(PCBM)/ITO exhibited a low-voltage operating flash type memory capability.

Keywords Donor-σ-acceptor; organic memory; PCBM; PDI; X-shaped molecule

Introduction

Organic semiconductors are capable of tuning absorption and emission properties and the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) molecular energy levels by controlling molecular architecture. They stimulate the synthesis of various molecular architectures by combining electron-donating and electron-accepting moieties through a covalent bond, and they show the transfer of one electron from the donor unit to the acceptor unit by applying electrical and photo-excitation [1–4]. Donor and acceptor molecules that are combined to prepare donor-σ-acceptor (D-σ-A) molecules through the σ-bond are promising candidates for the construction of molecular rectifiers,[5,6] programmable digital memory, [7–9] and organic solar cells [10,11] In particular, there is much interest in the development of new organic switching materials that satisfy the requirements of non-volatile and volatile memory devices including electron donor/acceptor molecules and polymers. Organic materials sandwiched between two vertically aligned electrodes constitute a memory device design possessing at least two stable resistance states that can be modulated by external electrical field.

In typical donor-acceptor combined system, charge transfer (CT) occurs and electrical charges are partially transferred from the donor to the acceptor moiety. [12–15] Electric

*Address correspondence to Dong Hoon Choi, Department of Chemistry, Research Institute for Natural Sciences, Korea University, Seoul 136-701, South Korea. E-mail: dhchoi8803@korea.ac.kr

field-induced CTs are expected to occur in the intra- and intermolecular CT complexes, which is closely related with the molecular association behaviors in the solid state. As electron acceptors, perylene diimide (PDI) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) are well-known n-type semiconducting molecules that are suitable for applications to thin film transistors, organic solar cells, and resistive random access memory (RRAM). [16] In this study, an anthracene-based X-shaped semiconducting molecule was selected as a donor moiety to anchor with the electron acceptor. The anthracene-based donor was found to be a good p-type semiconductor, showing high carrier mobility of around 0.1 $\sim$ 0.3 $cm^2\ V^{-1}s^{-1}$[17].

The synthesized two molecules with A-σ-D-σ-A type were employed to fabricate the sandwiched memory devices for studying their electrical bistability. The memory devices with the configuration of Al/(HAT)-2(PDI) or (HAT)-2(PCBM)/ITO exhibited a low-voltage operating flash type memory capability.

Experimental Section

Instrumentation

The redox properties of two molecules were examined by using cyclic voltammetry (Model: EA161 eDAQ). Thin films were coated on a platinum plate using chloroform as a solvent. The electrolyte solution employed was 0.10 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in a freshly dried acetonitrile. The Ag/AgCl and Pt wire (0.5 mm in diameter) electrodes were utilized as reference and counter electrodes, respectively. All measured potentials reported were referenced to an Fc/Fc^+ standard. The scan rate was at 50 mV/s.

In order to study absorption behavior, the films of two molecules were fabricated on quartz substrates as follows. The solution (1 wt%) of each molecule in chloroform was filtered through an acrodisc syringe filter (Millipore 0.45 μm) and subsequently spin-cast on the quartz glass. The films were dried overnight at 50°C for 24 hours under vacuum. Absorption spectra of samples in a film and solution state (chloroform, conc. 1×10^{-5} mole/L) were obtained using a UV-Vis spectrometer (HP 8453, photodiode array type) in the wavelength range of 190–1100 nm.

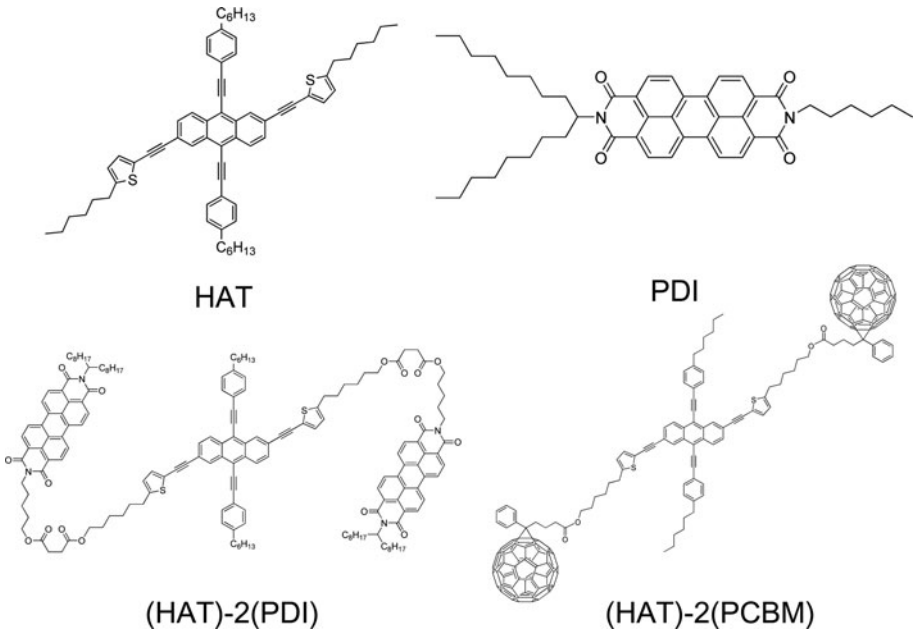
Fabrication and Electrical Characterization of Memory Devices

The indium-tin oxide (ITO, 100 nm in thickness) coated onto glass substrate was used as a bottom electrode. The ITO surface was cleaned sequentially with deionized water, acetone and isopropanol by sonication for 10 min. Subsequently, a solution of the molecules (5 mg /mL) filtered through Acrodisc membrane microfilters with a pore size of 0.45 μm was spin-coated onto the ITO substrate at a rate of 2000 rpm for 60 s. The films were dried under vacuum at 50°C for 6 hrs. The thickness of the molecular layer was about 45 nm, as determined by the Surface Profiler (Tencor P10).

Finally, an Al top electrode with an area of 0.785 mm^2 and a thickness of about 100 nm was formed by thermal evaporation onto the film surface through a shadow mask. All electrical measurements of the devices were characterized under ambient conditions using a Keithley 4200-SCS semiconductor parameter analyzer.

Results and Discussion

We demonstrated the interesting A-σ-D-σ-A type molecules whose syntheses were described in our previous literature [18] (see Scheme I).



Scheme 1. Structures of HAT, PDI, and A-σ-D-σ-A type molecules bearing HAT.

The π-conjugated core unit, 5,5′-(9,10-bis((4-hexylphenyl)ethynyl)anthracene-2,6-diyl)bis(ethyne-2,1-diyl)bis(2-hexylthiophene) (HAT) contains thiophene and phenyl units in four peripheral arms. We found that the hexyl side group in HAT enhances not only the solubility but also the degree of self-organization (i.e., molecular ordering).

The absorption spectra of (HAT)-2(PDI)s and (HAT)-2(PCBM)s were recorded in both solution (conc. 1×10^{-5} M in $CHCl_3$) and film states. The solution of molecule, (HAT)-2(PDI) exhibited a typical singlet transition in the range of 410–570 nm with a well-resolved vibronic structure. (Figure 1A, curve (a)) The spectrum of (HAT)-2(PDI) molecule in Figure 1A revealed that coupled compounds exhibit $\pi - \pi^*$ energy transitions in the individual spectrum. The absorption spectrum of (a) for the molecules in solution state

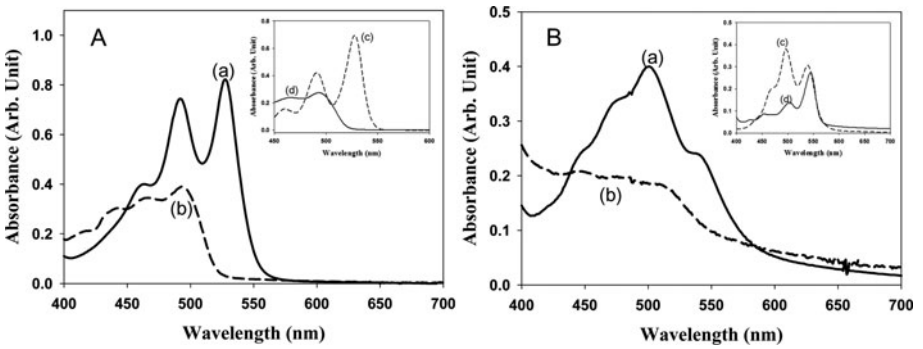


Figure 1. Absorption spectra of synthesized molecules in solution state (A) and in as-spun film state (B): (a) (HAT)-2(PDI), (b) (HAT)-2(PCBM), (c) PDI, (d) HAT.

revealed characteristic bands with maxima at 528 and 493 nm, attributed to the presence of the PDI groups. (see inset, curve (c)).

(HAT)-2(PCBM) exhibited spectral behaviour almost identical to HAT, showing peaks at 494 and 466 nm in the solution state. (see the spectrum (d)) Figure 1B shows the absorption spectra of the molecules in the thin film states. The thin-film-state spectrum of (HAT)-2(PDI) was broader than the solution-state spectra and a weak shoulder band was observed at 540 nm in the former spectra, indicating that the J-aggregation behavior in HATs was almost disrupted [19] (see inset, curve (d)), The absorption spectrum of (HAT)-2(PCBM) did not exhibit a J-aggregation band either; however, they exhibited significant spectral broadening due to the formation of CT complex.

The electrochemical properties of (HAT)-2(PDI) and (HAT)-2(PCBM) films were probed by cyclic voltammetry in a three-electrode cell setup. (HAT)-2(PDI) has oxidation and reduction potentials of 1.12 and −0.60 eV yielding −5.46 eV of HOMO and −3.70 eV of LUMO energy, respectively. (HAT)-2(PCBM) has an oxidation and reduction potentials of 1.08 and −0.49 eV yielding −5.37 eV of HOMO and −3.82 eV of LUMO energy. The HOMO levels of two molecules is very similar to that of HAT; The LUMO levels are also similar to PDI or PCBM. Although two opposite electroactive moieties were bound together, the HOMO-LUMO levels did not change significantly [E_{HOMO} of HAT = −5.35 eV]; this implies that the two moieties were isolated well enough to limit their mutual interaction between donor and acceptor units even in the solid state.

The measured and calculated parameters representing the physical properties were tabulated in Table 1. Eventually, the potential applicability of the newly synthesized molecules as electroactive materials in a memory device was investigated. Using the combined molecules of donor and acceptor, we can apply them to resistive random access memory (RRAM). It was so intriguing that the sandwiched devices based on nano-scale thin films demonstrated unique digital memory characteristics. The memory effect of two molecules was revealed by the current–voltage (I–V) measurements of an Al/A-σ-D-σ-A molecule/ITO structure. Representative I–V curves of the memory devices fabricated with (HAT)-2(PDI) (a) and (HAT)-2(PCBM) (b) were shown in Figure 3. During voltage sweeping from 0 to +5.0 V, the resulting current exhibits a sharp increase by 6 orders of magnitude at +2.5 V in Figure 3A. This indicates that the device is switched from a low conductivity state (OFF-state) to a high conductivity state (ON-state), which is equivalent to a "writing" process in a digital memory cell. When the voltage is swept backward from −5.0 V to 0 V

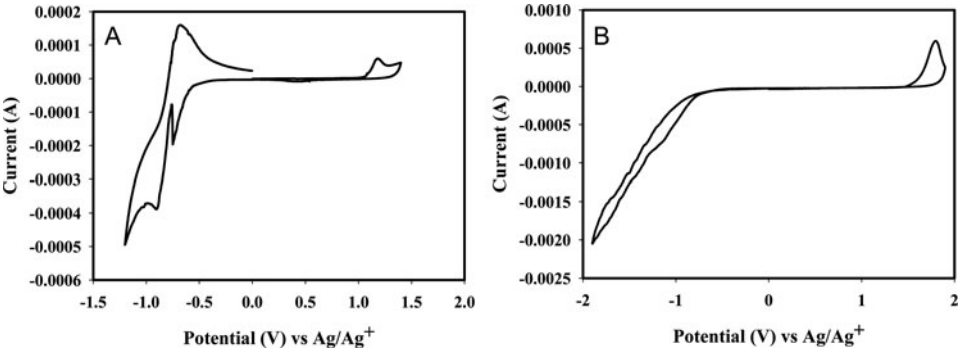


Figure 2. Cyclic voltammograms of two molecules. (A) (HAT)-2(PDI), (B) (HAT)-2(PCBM). *Sample: film on Pt electrodes.

Table 1. Measured and calculated parameters of D-σ-A molecules

Molecule	T_m (°C)	T_d (°C)	$\lambda_{max.}^{abs.}$ (nm)[a]	$\lambda_{max.}^{PL.}$ (nm)[a]	$\lambda_{max.}^{abs.}$ (nm)[b]	E_{ox}^{onset} (V)	E_{red}^{onset} (V)	HOMO (eV)[c]	LUMO (eV)[c]	E_g^{elec} (eV)[c]
(HAT)-2(PDI)	100	404	492,527	537,576	498,538	1.12	−0.60	−5.46	−3.70	1.76
(HAT)-2(PCBM)	—	396	466,494	517,553	442,508	1.08	−0.49	−5.37	−3.82	1.55

[a]Measured in chloroform with a concentration of 10^{-5} M.
[b]Films were spin-coated from chloroform solution.
[c]The values were obtained from cyclic voltammograms. Fc/Fc^+ standard.
*Sample: film on Pt electrode.

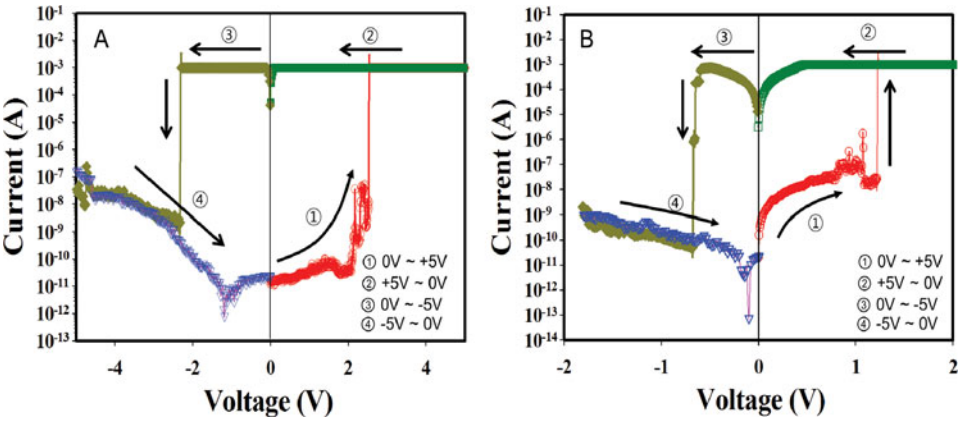


Figure 3. Current–voltage (I–V) characteristics of Al/(HAT)-2(PDI)/ITO (A) and Al/(HAT)-2(PCBM)/ITO (B) devices with an electrode area of 0.785 mm^2.

and from zero to −5.0 V, the device still showed on-state current. However, the resultant current decreases abruptly by 6 orders of magnitude when the voltage is increased up to −2.3 V. This indicates that the device is restored to an original low conductivity state, which corresponds to the "erasing" process for the memory device.

Two molecules showed common behaviors of flash-type memory. The fabricated devices showed low turn-on threshold voltages of +2.5 V ((HAT)-2(PDI)) and +1.2 V ((HAT)-2(PCBM)) and both ON/OFF current ratios on the order of $>10^5 \sim 10^6$. The conductivity transition is mainly attributed to electric field induced CT and charge trapping-detrapping, which is a recognized mechanism of bistable switching behavior in A-σ-D-σ-A molecules and polymers [7]. The interaction between HAT and corresponding acceptor in each molecule may be weak before electronic transition, so that the film had a low conductivity. A high electric field may facilitate charge transfer from the HOMO of HAT and LUMO of PDI (or PCBM). Consequently, the HOMO of HAT and LUMO of PDI (or PCBM) become partially filled, and HAT and acceptor are charged positively and negatively, respectively. Therefore, carriers are generated and the device exhibits a sharp increase in conductivity after the CT process.

The retention behaviors of the ON/OFF states for the Al/(HAT)-2(PDI) or (HAT)-2(PCBM)/ITO memory devices are shown in Figure 4. It is found that the memory cells exhibited two stable states of ON and OFF within 1000 sec. In the device with Al/(HAT)-2(PDI)/ITO, ON and OFF current ratio was sustained to be around 10^7 under applying +3.0 V. The device with Al/(HAT)-2(PCBM)/ITO showed almost identical ON/OFF current ratio even under applying +1.5 V. Although the measurement time is limited to 1000 sec, no serious modulation behavior of ON and OFF current was observed. It could be thought that the resistance of high conductivity state in (HAT)-2(PCBM) is much lower than that of (HAT)-2(PDI).

In brief, the stability of charge trapping and CT complex between donor and acceptor moieties govern the type of memory device. The volatile nature in the devices is due to the presence of the shallow trapped charges with spontaneous backward transfer of charge carriers when the electric field was removed. On the contrary, non-volatile flash memory behaviors in this study might be due to high density of electron accepting moiety. Under the preliminary experiment, electrical switching characteristics of write-read-erase-read

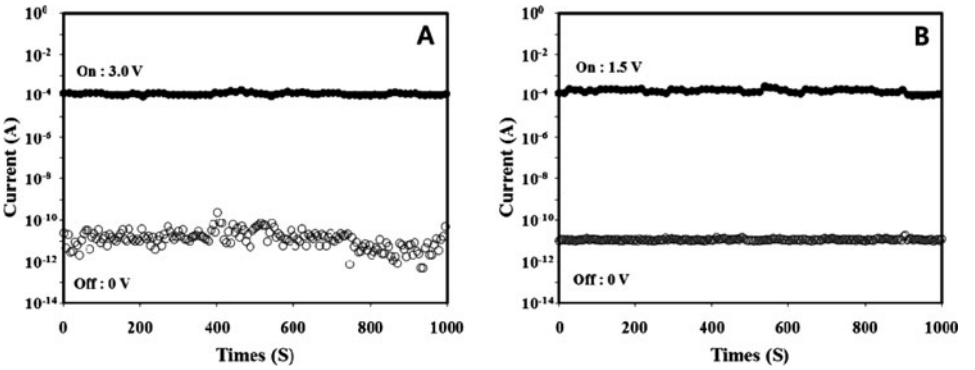


Figure 4. Retention characteristics of on and off states for the devices with (HAT)-2(PDI) (A) and (HAT)-2(PCBM) (B) at room temperature.

cycles and retention time at elevated temperature will be further studied using new D-σ-A molecules.

Conclusion

A-σ-D-σ-A molecules were successfully synthesized and applied them to electrically bistable memory devices with simplified device configuration. To our knowledge, the A-σ-D-σ-A molecules used in this study suggested new concept of promising candidates for next-generation (non-)volatile memory devices. Stability of the encoded information and detailed mechanism based on the trapping-detrapping and electric field induced charge transfer effect will be investigated further.

Acknowledgments

This research was supported by National Research Foundation of Korea (NRF2012R1A2A 1A01008797 & 20110026418) and by Key Research Institute Program through the NRF funded by the Ministry of Education, Science and Technology (NRF20100020209).

References

[1] Liddell, P. A., Kodis, G., Moore, A. L., Moore, T. A., & Gust, D. (2002). *J. Am. Chem. Soc.*, *124*, 7668.
[2] Oike, T., Kurata, T., Takimiya, K., Otsubo, T., Aso, Y., Zhang, H., Araki, Y., & Ito, O. (2005). *J. Am. Chem. Soc.*, *127*, 15372.
[3] Lor, M., Thielemans, J., Viaene, L., Cotlet, M., Hofkens, J., Weil, T., Hampel, C., Müllen, K., Verhoeven, J. W., Van der Auweraer, M., & De Schryver, F. C. (2002). *J. Am. Chem. Soc.*, *124*, 9918.
[4] Peeters, E., van Hal, P. A., Meskers, S. C. J., Janssen, R. A. J., & Meijer, E. W. (2002). *Chem. Eur. J.*, *8*, 4470.
[5] Stokbro, K., Taylor, J., & Brandbyge, M. (2003). *J. Am. Chem. Soc.*, *125*, 3674.
[6] Ho, G., Heath, J. R., Kondratenko, M., Perepichka, D. F., Arseneault, K., Pézolet, M., & Bryce, M. R. (2005). *Chem. Eur. J.*, *11*, 2914.
[7] Lee, W.-Y., Kurosawa, T., Lin, S.-T., Higashihara, T., Ueda, M., & Chen, W.-C. (2011). *Chem. Mater.*, *23*, 4487.

[8] Fang, Y.-K., Liu, C.-L., Yang, G.-Y., Chen, P.-C., & Chen, W.-C. (2011). *Macromolecules*, *44*, 2604.
[9] Fang, Y.-K., Liu, C.-L., Li, C., Lin, C.-J., Mezzenga, R., & Chen, W.-C. (2010). *Adv. Funct. Mater.*, *20*, 3012.
[10] Nishizawa, T., Tajima, K., & Hashimoto, K. (2007). *J. Mater. Chem.*, *17*, 2440.
[11] Mi, B., Dong, Y., Li, Z., Lam, J. W. Y., Häußler, M., Sung, H. H. Y., Kwok, H. S., Williams, I. D., Liu, Y., Luo, Y., Shuai, Z., Zhu, D., & Tang, B. Z. (2005). *Chem. Commun.*, 3583.
[12] Chu, C. W., Ouyang, J., Tseng, J. H., & Yang, Y. (2005). *Adv. Mater.*, *17*, 1440.
[13] Liu, G., Ling Q.-D., Kang, E.-T., Neoh, K.-G., Liaw, D.-J., Chang, F.-C., Zhu, C.-X., & Chan, D. S. H. (2007). *J. Appl. Phys.*, *102*, 024502.
[14] Song, Y., Ling, Q. D., Lim, S. L., Teo, E. Y. H., Tan, Y. P., Li, L., Kang, E. T., Chan, D. S. H., & Zhu, C. (2007). *IEEE Electron Device Lett.*, *28*, 107.
[15] Potember, R. S., Poehler, T. O., & Cowan, D. O. (1979). *Appl. Phys. Lett.*, *34*, 405.
[16] Li, J., Dierschke, F., Wu, J., Grimsdale, A. C., & Müllen, K. (2006). *J. Mater. Chem.*, *16*, 96.
[17] (a) Jung, K. H., Bae, S. Y., Kim, K. H., Cho, M. J., Lee, K., Kim, Z. H., Choi, D. H., Lee, D. H., Chung, D. S., & Park, C. E. (2009). *Chem. Commun.*, 5290. (b) Kim, M. H., Cho, M. J., Kim, K. H., Hoang, M. H., Lee, T. W., Jin, J.-I., Kang, N. S., Yu, J.-W., & Choi, D. H. (2009). *Org. Electron.*, *10*, 1429.
[18] Shin, J., Lee, T. W., Kang, N. S., Kim, K. H., Hong, J.-M., & Choi, D. H. (2012). *Synth. Met.*, *162*, 1335.
[19] Kim, K. H., Bae, S. Y., Kim, Y. S., Hur, J. A., Hoang, M. H., Lee, T. W., Cho, M. J., Kim, Y., Kim, M., Jin, J.-I., Kim, S.-J., Lee, K., Lee, S. J., & Choi, D. H. (2011). *Adv. Mater.*, *23*, 3095.