Molecular Crystals and Liquid Crystals

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

Introduction of Interlayer via Oxetane Based Crosslinking Method for Blue Polymer Light-Emitting Diode Applications

Won Suk Shin [a], Sung Chul Kim [b], Eun-Jae Lee [b], Sung-Min Park [b], Sung-Ho Jin [a b], Jae Wook Lee [c] & Yeong-Soon Gal [d]

[a] Center for Plastic Information System, Pusan National University, Busan, Korea

[b] Department of Chemistry Education and Interdisciplinary Program of Advanced Information and Display Materials, Pusan National University, Busan, Korea

[c] Department of Chemistry, Dong-A University, Busan, Korea

[d] Polymer Chemistry Lab., Kyungil University, Hayang, Korea

Version of record first published: 22 Sep 2010

To cite this article: Won Suk Shin, Sung Chul Kim, Eun-Jae Lee, Sung-Min Park, Sung-Ho Jin, Jae Wook Lee & Yeong-Soon Gal (2007): Introduction of Interlayer via Oxetane Based Crosslinking Method for Blue Polymer Light-Emitting Diode Applications, Molecular Crystals and Liquid Crystals, 471:1, 335-343

To link to this article: http://dx.doi.org/10.1080/15599610701548944

Mol. Cryst. Liq. Cryst., Vol. 471, pp. 335–343, 2007

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15599610701548944

Taylor & Francis
Taylor & Francis Group

Introduction of Interlayer via Oxetane Based Crosslinking Method for Blue Polymer Light-Emitting Diode Applications

Won Suk Shin
Center for Plastic Information System, Pusan National University, Busan, Korea

Sung Chul Kim
Eun-Jae Lee
Sung-Min Park
Department of Chemistry Education and Interdisciplinary Program of Advanced Information and Display Materials, Pusan National University, Busan, Korea

Sung-Ho Jin
Center for Plastic Information System and Department of Chemistry Education and Interdisciplinary Program of Advanced Information and Display Materials, Pusan National University, Busan, Korea

Jae Wook Lee
Department of Chemistry, Dong-A University, Busan, Korea

Yeong-Soon Gal
Polymer Chemistry Lab., Kyungil University, Hayang, Korea

Two interlayers, blended interlayer based on **TPD-oxetane** *with* **PFO-TPD-OCH_3** *and crosslinkable polymer interlayer based on* **Poly(RO_2-spiro-TPA-oxetane)**, *were introduced in polymer light-emitting diodes (PLEDs). Both interlayers showed resistance to organic solvents and the performance of PLEDs was greatly enhanced when each interlayer was inserted. The maximum*

This research was supported by the University IT Research Center (ITRC) Project of the Ministry of Information and Communication (J. W. Lee) and the National Research Laboratory (NRL) program of KOSEF (S. H. Jin).

Address correspondence to Sung-Ho Jin, Department of Chemistry Education and Center for Plastic Information System, Pusan National University, Busan 609-735, Korea. E-mail: shjin@pusan.ac.kr

luminescence efficiency of 0.147 cd/A at 11 V and the maximum luminescence of 739 cd/m^2 at 15 V have been achieved with blue light emitting polymer, **Poly(RO_2-spirobifluorene)**.

Keywords: crosslinking; interlayer; oxetane; PLED

INTRODUCTION

After nearby two decades of development, LEDs derived from π-conjugated polymers have now reached the stage of commercialization, as small-sized flat-panel displays [1]. To achieve optimum device performance, it is desirable to have multilayer structures having discrete-hole transport layer (HTL), emissive layer (EML), and electron transport layer (ETL) functions. The role of HTL is not only to maximize hole injection from the anode, but also to block efficiency-depleting electron overflow from, and to confine excitons within, the EML [2]. With such multilayer structures, high performance devices have been realized for small molecule based organic light-emitting diodes (OLEDs) fabricated via vacuum deposition. Compared to its small molecule counterparts, a multilayer PLED is far more challenging to fabricate due to the risk of partially dissolving a previous layer while depositing the next in solution casting processes. To overcome this risk by introducing insoluble HTLs, the crosslinking method after depositing crosslinkable precursors is the most promising one to introduce organic insoluble HTLs [2–7]. In this article, two different types of interlayer based on oxetane were introduced through crosslinking method as an extension of new high performance HTLs and their PLED performances with poly(spirobifluorene) as an emitting layer characterized.

EXPERIMENTAL

Synthesis and Preparation of Materials

Synthesis of N,N′-di(4-(6-(3-ethyloxetane-3-yl-methoxy))hexyloxyphenyl) N,N′-diphenylbenzidine (**TPD-oxetane**): A mixture of diphenybenzidine (1.09 g, 3.23 mmol), 3-(6-(4-iodophenoxy) hexyloxymethyl)-3-methyloxetane (3.3 g, 8.07 mmol), KOH (2.4 g, 42.8 mmol), cuprous chloride (0.147 g), and 1,10-phenanthroline (0.08 g) in toluene (20 ml) was refluxed at 125°C for 20 h. The formed water was removed with a fixed Dean-Stark trap. After the reaction, the mixture was cooled to room temperature, poured into 300 ml water, extracted with $CHCl_3$.

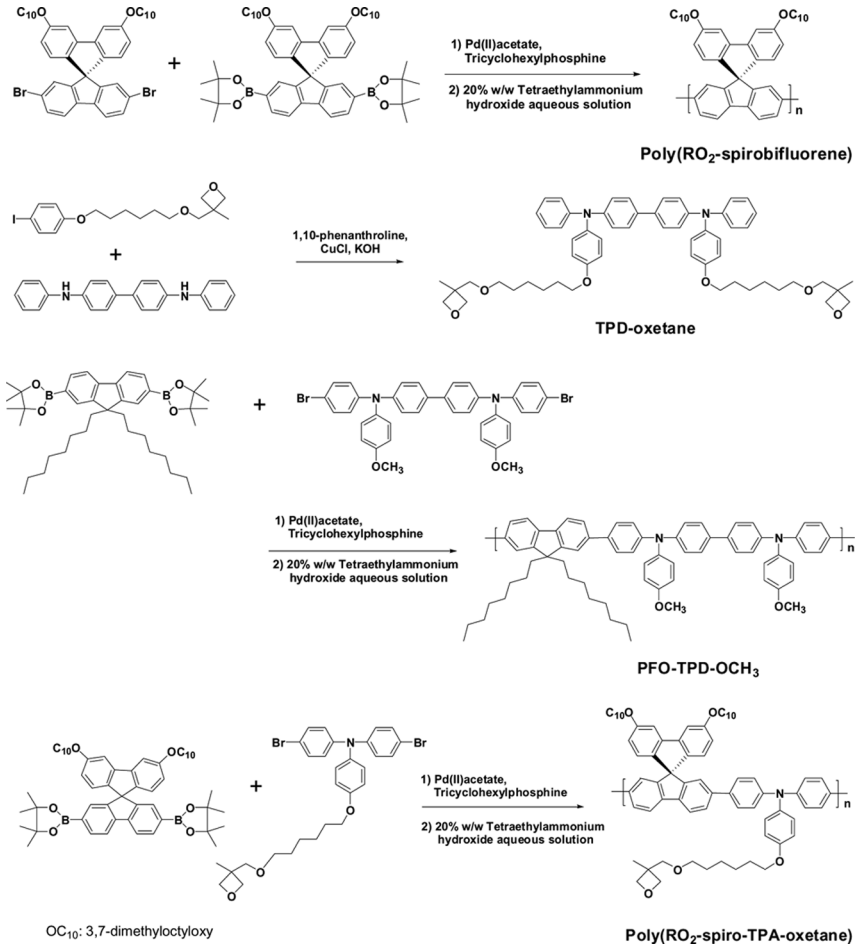
The organic layer was washed with a dilute solution of ammonium hydroxide and water successively, dried with anhydrous $MgSO_4$ and evaporated. Purification by silica column chromatography (hexane: ethyl acetate = 7:2) to give a yellow liquid product, N,N′-di(4-(6-(3-ethyloxetane-3-yl-methoxy))hexyloxyphenyl) N,N′-diphenylbenzidine (1.4 g, yield: 50%). ^{1}H-NMR ($CDCl_3$, δ ppm): 7.48–7.32(br, 4H), 7.26–7.16 (br, 4H), 7.16–6.90 (br, 14H) 6.90–6.76 (br, 4H), 4.50–4.48 (d, J = 5 Hz 2H), 4.35–4.33 (d, J = 5 Hz, 2H), 3.92–3.87 (t, J = 6 Hz, 2H), 3.48–3.43 (m, 4H) 1.81–1.27 (m, 11H). ^{13}C-NMR ($CDCl_3$): δ (ppm) 156.05, 148.30, 147.22, 140.72, 134.27, 129.33, 127.59, 127.32, 123.24, 123.09, 122.16, 115.61, 80.45, 76.36, 71.73, 68.35, 40.19, 29.76, 29.57, 26.225, 21.65.

Synthesis of poly(3′,6′-bis(3,7-dimethyloctyloxy)-9,9́-spirobifluorene-2,7-diyl) (**Poly(RO_2-spirobifluorene)**): To a dried 3-neck round bottom flask, 2,7-dibromo-3′,6′-bis(3,7-dimethyl-octyloxy)-9,9′-spirobifluorene (0.22 g, 0.28 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-3′,6′-bis(3,7-dimethyloctyloxy)-9,9′spiro-bifluorene (0.25 g, 0.28 mmol), palladium(II) acetate (1.6 mg, 2 mol%) and tricyclohexylphosphine (6.4 mg, 8 mol%) under nitrogen atmosphere were added. Dried toluene (3 ml) was added and the mixture was stirred at 90°C for 5 min. 20% w/w Tetraethylammonium hydroxide aqueous solution (2.3 ml) was added and the mixture was stirred for 1.5 days. To this mixture anthracenylboronic acid (0.05 g) was added, and after stirring another 2 h, bromoanthracene (0.12 g) was added for end capping the polymer chain. After stirring for further 4 h, the polymerization solution was poured into 300 ml of methanol, and the crude polymer was successively Soxhlet extracted with methanol and acetone to remove the unreacted monomers, impurities, and oligomers. The polymerization solution was filtered through silica plug, and the resulting polymer was redissolved in chloroform and reprecipitated in methanol (300 ml) under stirring. The precipitated product was filtered and then dried in vacuuo to give the white solid product (0.21 g, yield: 60%). Mw = 16,000 g/mole, PDI = 1.77, Tg = 293°C and 5% weight loss under N_2 was obserbed at 415°C. ^{1}H-NMR ($CDCl_3$, δ ppm): 6.40–6.70 (br, 6H), 6.70–6.85 (br, 3H), 7.18–7.4 (br, 7H), 7.45–7.8 (br, 3H), 3.8–4.2 (br, 4H), 1.95–0.6 (br, 76H).

Poly{9,9′-dioctylfluorene-2,7-diyl-*co*-*N*,*N*′-diphenyl-*N*,*N*́-bis(4-methoxyphenyl)benzidine -4′,4′-diyl} (**PFO-TPD-OCH$_3$**) and poly{3′,6′-bis(3,7-dimethyloctyloxy)-9,9′-spirobifluorene-2,7-diyl-*co*-4-(6-((3-methyloxetan-3-yl)methoxy)hexyloxyphenyl-bisphenylamine-4′,4′-diyl)} (**Poly(RO_2-spiro-TPA-oxetane)**) were synthesized using a similar method used for the preparation of **Poly(RO_2-spirobifluorene)**.

PFO-TPD-OCH$_3$: yield 25%, Mw = 89,000 g/mole, PDI = 2.28, Tg = 136°C and 5% weight loss under N_2 was obserbed at 385°C. ^{1}H-NMR ($CDCl_3$, δ ppm): 6.45–7.9 (br, 38H), 3.4–3.9 (br, 7H), 2.2–1.7 (br, 4H), 1.4–0.4 (61H). Anal Calcd for $(C_{67}H_{72}N_2O_2)_n$: C, 85.85; H, 7.74; N, 2.99; O, 3.41. Found: C, 83.64; H, 7.84; N, 2.92; O, 2.99.

Poly(RO$_2$-spiro-TPA-oxetane): yield 41%, Mw = 27,000 g/mole, PDI = 2.10, Tg = 146°C and 5% weight loss under N_2 was obserbed at 369°C. ^{1}H-NMR ($CDCl_3$, δ ppm): 6.6–7.1 (br, 13H), 7.3 (br, 3H),



SCHEME 1 Synthetic route.

7.5–7.9 (br, 2H), 4.5 (2H), 4.35 (2H), 4.1–4.0 (br, 4H), 3.9 (2H), 3.5 (4H), 1.9–0.7 (br, 65H).

Introduction of Interlayer

Blended interlayer (**BIL**) based on **PFO-TPD-OCH$_3$** and **TPD-oxetane**: 1.5 wt % solutions of each **TPD-oxetane** and **PFO-TPD-OCH$_3$** were prepared with anhydrous toluene and then blended in 1:1 weight ratio. 1 wt% of PAG (photoacid generator, relative to the TPD-oxetane) was added to this blend solution and then spin-coated onto indium-tin oxide (ITO) substrate or on PEDOT:PSS layer to get 40 nm thickness of pristine film. The film was irradiated with UV lamp for 30 sec and annealed at 180°C for 10 min. Then, the film was washed several times with chlorobenzene and annealed at 180°C for 2–3 min yielded the desired interlayer film with 10 nm thickness. The resulting polymer network was found to be insoluble in many common solvents. The films exhibited an average surface roughness (rms roughness) of about 1.5 nm determined by atomic force microscopy (AFM).

Crosslinkable polymer interlayer (**CPL**) based on **Poly(RO$_2$-spiro-TPA-oxetane)**: 2 wt% **Poly(RO$_2$-spiro-TPA-oxetane)** solution in anhydrous toluene was prepared and then blended with 1 wt% of PAG (relative to the polymer) prior to spin-coating onto ITO substrate or on PEDOT:PSS layer. Afterward, similar procedure as that of **BIL** was followed to obtain insoluble interlayer.

LED Fabrication

Electroluminescent devices were prepared and investigated as sandwiched structures between calcium and ITO electrodes. Glass substrate coated with ITO, whose conductivity was about 15 Ω/square (from Samsung Corning) served as anode electrode. The PEDOT:PSS (30 nm) as a hole injection layer was spin-coated from aqueous solution with 10 wt% of isopropyl alcohol. Then an insoluble interlayer was introduced as explained above. The thickness of interlayer was around 10 nm. For an emissive layer (EML), 1.5 wt% **Poly(RO$_2$-spirobifluorene)** solution prepared in chlorobenzene was spin-coated uniformly after filtering through 0.45 μm PP syringe filters. The thickness of EML was maintained in between 80 to 110 nm. The film thickness was measured by an alpha-step surface profiler (KLA-Tencor) with an accuracy of $\pm$ 1 nm. Finally, cathode electrode, LiF (1 nm)/Ca (20 nm)/Al (200 nm) was vacuum (1×10^{-6} torr) evaporated onto the emissive layer. The active area of the device was approximately 4 mm^2. Current density-voltage-luminescence (*J-V-L*) characteristics

were measured using a current/voltage source (Keithly 236) and an optical power meter (CS-1000, LS-100). Some devices were made by excluding either PEDOT:PSS layer or interlayer to compare the effect of each layer.

RESULTS AND DISCUSSION

Crosslinking method was applied to make the interlayer resistant to the organic solvents, which is used for next film coating. Here, we introduced two types of conjugated polymer based interlayers, **BIL** based on **PFO-TPD-OCH$_3$** and **TPD-oxetane** and **CPL** based on **Poly(RO$_2$-spiro-TPA-oxetane)**, between PEDOT:PSS and an emissive **Poly(RO$_2$-spirobifluorene)** layer. After full procedure of interlayer introduction, no further interlayer film thickness losses or UV-visible absorption spectrum changes were detected as shown in Figure 1.

HOMO and LUMO levels of polymers were measured using cyclic voltammetry (CV) and optical absorption edge, which are depicted at Figure 2(a). Two interlayer polymers, **PFO-TPD-OCH$_3$** and **Poly(RO$_2$-spiro-TPA-oxetane)**, showed HOMO levels of 5.03 and 5.30 eV, respectively. These values are good enough for hole injection from PEDOT:PSS to **Poly(RO$_2$-spirobifluorene)** emitting layer since the HOMO levels of two interlayer polymers are in between the work function of PEDOT (5.0 eV) and HOMO level of **Poly(RO$_2$-spirobifluorene)** (5.51 eV). In addition to the suitable HOMO levels, triphenylamine containing polymers are well known for hole transporting materials with high hole mobility [8,9]. With well balanced HOMO levels and high hole mobility properties, interlayer can enhance hole injection and hole transporting ability. The high LUMO levels of **Poly(RO$_2$-spiro-TPA-oxetane)** and **PFO-TPD-OCH$_3$** compared with the LUMO level of EML can attribute for the block of the quenching of radiative excitions by PEDOT:PSS and thus remove a nonradiative chanel introduced by PEDOT:PSS [10].

To investigate the Electroluminescence (EL) properties of multilayer device with **BIL** and **CPL**, the PLED devices with three different structures were fabricated and their EL performances were summarized in Table 1. **Poly(RO$_2$-spirobifluorene)** was used as an EML and three different types of devices were 1) ITO/PEDOT/EML/LiF/Ca/Al (**device a**), 2) ITO/Interlayer/EML/LiF/Ca/Al (**device b** and **d**) and 3) ITO/PEDOT/Interlayer/EML/LiF/Ca/Al (**device c** and **e**), respectively. When we inserted interlayer, the PLED performance was strongly enhanced than the device without interlayer. Device efficiency was increased from 0.062 cd/A at 11 V in **device a** to

TABLE 1 EL Performance of ITO/PEDOT:PSS/Interlayer (10 nm)/EML (80 nm)/LiF (0.7 nm)/Ca (20 nm)/Al (200 nm) Devices

Device	Interlayer (10 nm)	Buffer layer	Turn on (V)	L_{max}[a] (cd/m^2)	LE_{max}[b] (cd/A)
a	–	PEDOT:PSS	5	311 (at 11 V)	0.062 (at 11 V)
b	BIL[c]	–	5	327 (at 16 V)	0.080 (at 9 V)
c	BIL[c]	PEDOT:PSS	5	388 (at 15 V)	0.147 (at 11 V)
d	CPL[d]	–	7	273 (at 16 V)	0.043 (at 16 V)
e	CPL[d]	PEDOT:PSS	7	739 (at 15 V)	0.131 (at 17 V)

[a]Maximum luminescence
[b]Maximum luminescence efficiency
[c]Blended interlayer based on **TPD-oxetane:PFO-TPD-OCH$_3$** = 1:1 mixture
[d]Crosslinkable polymer interlayer based on **Poly(RO$_2$-spiro-TPA-oxetane)**.

0.147 ca/A at 11 V in **device c** and to 0.13 cd/A at 17 V in **device e**. We believed that the introduction of interlayer can reduce the energy barrier between PEDOT and light emitting polymer, resulting an easy hole injection and the high LUMO level of interlayer can work as exciton blocking layer to increase the device efficiency. It is contributed that hole was injected from PEDOT to interlayer by almost ohmic contact. Since the morphology of interlayer was very smooth (r.m.s. roughness = 1.5 nm) the hole injected from PEDOT can easily move to the emissive layer [11]. To compare the hole transporting ability between PEDOT and each interlayer, we compared **device a**, **b** and **d**. In this experiment, the performance of **device b** was better

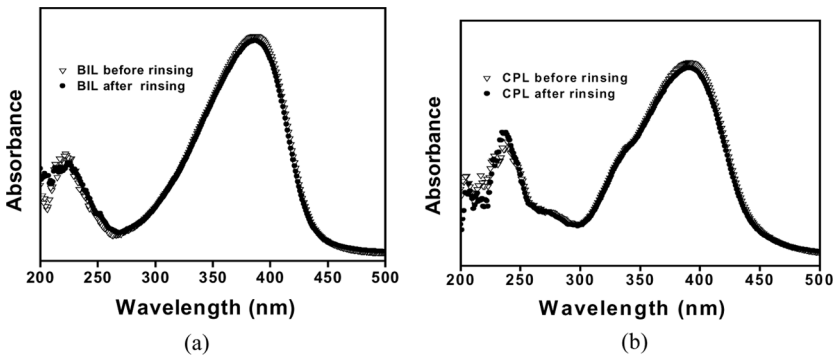


FIGURE 1 UV-visible absorption spectra of: (a) Blended interlayer (**BIL**) film based on **TPD-oxetane:PFO-TPD-OCH$_3$** = 1:1 mixture; (b) Crosslinkable polymer interlayer (**CPL**) film based on **Poly(RO$_2$-spiro-TPA-oxetane)**, before and after chlorobenzene spin rinsing.

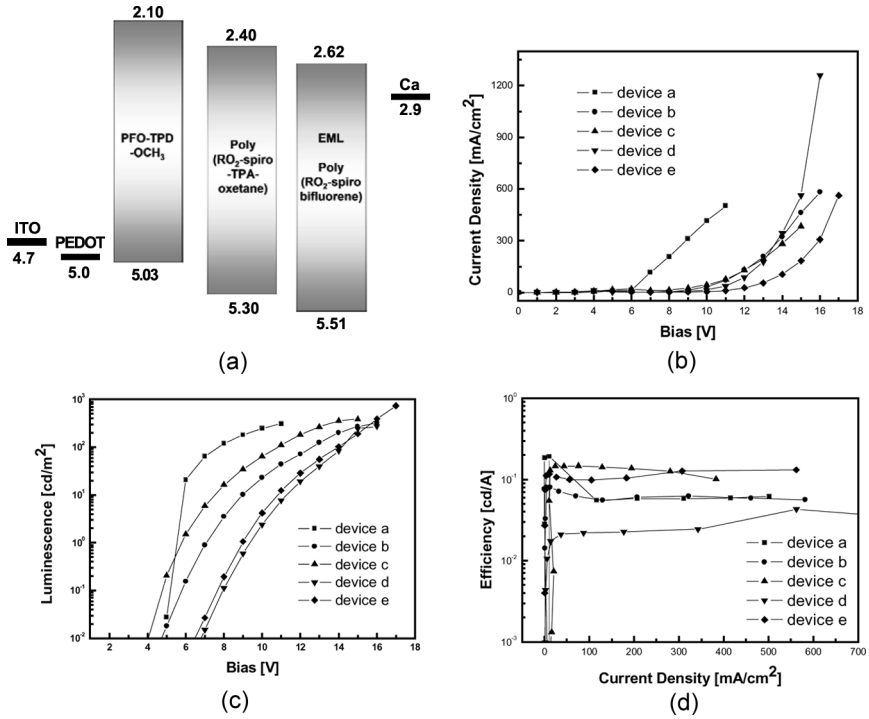


FIGURE 2 Work functions of synthesized polymers and J-V-L characteristics and efficiencies depend on device structures as summarized in Table 1.

than **device a**. From this data, we conclude that **PFO-TPD–OCH$_3$** effectively transferred the hole injected from PEDOT to the emissive layer. But, the performance of **device d** was less than **device a**. In the case of **device b**, **PFO-TPD-OCH3** polymer chain can be well stacked in film state due to the planar structure of fluorene backbone and the well stacked film can transfer charge more effectively via π-π overlapping. However, the structure of **Poly(RO$_2$-spiro-TPA-oxetane)** for **device d** is not planar because of orthogonally arranged spirobifluorene, it may reduce the charge transfer ability in interlayer.

CONCLUSIONS

We have developed two kinds of interlayer based on crosslinking method, which are blended interlayer with **TPD-oxetane** and **PFO-TPD-OCH$_3$** and crosslinkable polymer interlayer with **Poly(RO$_2$-spiro-TPA-oxetane)**. The devices, which including both PEDOT

and interlayer, showed better EL performances than the cases of single layer from one of PEDOT and interlayer. The maximum luminescence efficiency of 0.147 cd/A was observed with blended interlayer system at 11 V, while the maximum luminescence of 739 cd/m^2 was observed with crosslinkable polymer interlayer system at 15 V.

REFERENCES

[1] (a) Forrest, S. R. (2004). *Nature*, *428*, 911.
(b) Akcelrud, L. (2003). *Prog. Polym. Sci.*, *28*, 875.
[2] Yan, H., Lee, P., Armstrong, N. R., Graham, A., Evmenenko, G. A., Dutta, P., & Marks, T. J. (2005). *J. Am. Chem. Soc.*, *127*(9), 3172.
[3] David Müller, C., Falcou, A., Reckefuss, N., Rojahn, M., Wiederhirn, W., Rudati, P., Frohne, H., Nuyken, O., Becker, H., & Meerholz, K. (2003). *Nature*, *421*, 829.
[4] Bacher, E., Bayerl, M., Rudati, P., Reckefuss, N., Müller, C. D., Meerholz, K., & Nuyken, O. (2005). *Macromolecules*, *38*, 1640.
[5] Gong, X., Moses, D., Heeger, A. J., Liu, S., & Jen, A. K. Y. (2003). *Appl. Phys. Lett.*, *83*, 183.
[6] Bacher, A., Erdelen, C. H., Paulus, W., Ringsdorf, H., Schmidt, H. W., & Schuhmacher, P. (1999). *Macromolecules*, *32*, 4551.
[7] Klarner, G., Lee, J. I., Lee, V. Y., Chan, E., Chen, J. P., Nelson, A., Markiewicz, D., Siemens, R., Scott, J. C., & Miller, R. D. (1999). *Chem. Mater.*, *11*, 1800.
[8] Redecker, M., Bradley, D. D. C., Inbasekaran, M., Wu, W. W., & Woo, E. P. (1999). *Adv. Mater.*, *11*, 241.
[9] Kim, J.-S., Ho, P. K. H., Murphy, C. E., & Friend, R. H. (2004). *Macromolecules*, *37*, 2861.
[10] Kim, J.-S. & Friend, R. H. (2005). *Appl. Phys. Lett.*, *87*, 023506.
[11] Shi, Y., Liu, J., & Yang, Y. (2000). *J. Appl. Phys.*, *87*(9), 4254.