Flexible inverted polymer solar cells on polyethylene terephthalate substrate containing zinc oxide electron-collection-layer prepared by novel sol–gel method and low-temperature treatments

Takayuki Kuwabara [a,b,*], Tomoaki Nakashima [a], Takahiro Yamaguchi [a], Kohshin Takahashi [a,b,*]

[a] Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa, Ishikawa 920-1192, Japan
[b] Research Center for Sustainable Energy and Technology, Kanazawa University, Kakuma-machi, Kanazawa, Ishikawa 920-1192, Japan

ARTICLE INFO

ABSTRACT

Flexible and air-stable polymer solar cells were fabricated on a polyethylene terephthalate (PET) substrate. The cell structure was indium tin oxide (ITO) on PET/zinc oxide (ZnO)/ [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM):regioregular poly(3-hexylthiophene) (P3HT)/poly (3,4-ethylenedioxylenethiophene):poly(4-styrene sulfonic acid) (PEDOT:PSS)/Au, this being called the ZnO cell. Reproducible cell performances were obtained despite the ZnO cells being fabricated in air and at low temperature, using a novel ZnO precursor solution containing zinc(II) acetylacetonate as a metal source and acetylacetone as a Zn^{2+} complexing agent. The power conversion efficiency (PCE) of the flexible ZnO cells without sealing was 2.15% under irradiating AM1.5G simulated sunlight at 100 mW cm^{-2}. In addition, the performance of the non-sealed ZnO cells was almost constant in ambient atmosphere under continuous light irradiation for 100 h.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Bulk heterojunction polymer solar cells have the potential to provide low-cost, lightweight cells, and are easily scaled up using wet processes such as die coating, bar coating, ink-jet printing, and roll-to-roll printing techniques [1–4]. The organic active layer of polymer solar cells typically consists of a *p*-conjugated polymer donor and a fullerene derivative acceptor, and the power conversion efficiency (PCE) of polymer solar cells has recently achieved 6–8%. This has been driven by the development of new *p*-conjugated polymers [5–8] and fullerene derivatives [9,10]. In addition to increasing their efficiency, studies into their commercial viability (e.g. durability improvement, cost effective production of large scale flex-

ible cells, etc.) are very important. Especially, a main concern has been the stability of the organic solar cells [11,12].

We have developed inverted polymer solar cells with electron collection layers such as amorphous titanium oxide (TiO$_x$) [13–15], zinc oxide (ZnO) [16], and zinc sulfide [17]. We have previously reported the fabrication and the characterization of flexible polymer solar cells with a PET–ITO/sol–gel TiO$_x$/PCBM:P3HT/PEDOT:PSS/Au structure [18]. However, because the sol–gel TiO$_x$ precursor solution was unstable with respect to moisture, it was essential to handle the precursor solution in a N$_2$ filled glove box.

Several research groups have reported the fabrication of polymer solar cells on flexible substrates [19,20]. For example, a colloid solution containing ZnO nanoparticles has been used as the precursor to prepare the electron collection layer on PET and polyethylene naphthalate (PEN) [21,22]. However, the most well-known sol–gel ZnO films have not been used, because the films require heat treatment at much higher than 110 °C, which is the glass transition temperature of PET, in order to make the ZnO function as the electron collector. In this report, flexible

* Corresponding authors at: Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa, Ishikawa 920-1192, Japan. Tel.: +81 76 234 4770; fax: +81 76 234 4800.
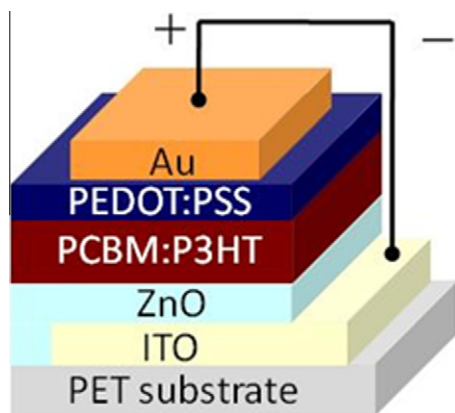*E-mail address:* tkuwa@t.kanazawa-u.ac.jp (T. Kuwabara).

Fig. 1. Device structure of the inverted polymer solar cells.

inverted polymer solar cells containing a thin ZnO layer were fabricated and characterized in air. The device structure is shown in Fig. 1. We report that a novel ZnO precursor solution, which contains zinc acetylacetate as the zinc source and acetylacetone as the complexing agent, makes it possible to prepare the ZnO film on flexible PET–ITO substrates at low temperatures and in air.

2. Experimental section

2.1. Materials

Zinc acetate ($Zn(OAc)_2$), zinc acetylacetate ($Zn(acac)_2$), acetylacetone (AA), monoethanolamine (MEA), 2-methoxyethanol, regioregular P3HT (Mw 87,000), PEDOT:PSS 1.3 wt.% dispersion in water, Triton-X 100, chlorobenzene (CB) and nitrobenzene (NB) were purchased from Sigma–Aldrich Chemical Co., Inc. PCBM was purchased from Frontier Carbon Corporation. All chemicals were used as received. Glass–ITO substrates (sheet *resistance* = 10 Ω/sq.) and Au wires were purchased from the Furuuchi Chemical Corporation. PET–ITO substrates (sheet *resistance* = 40 Ω/sq., thickness of PET sheet = 100 μm) were obtained from Reiko Co., Ltd.

2.2. Preparation of ZnO layers

The well-known ZnO precursor solution was prepared under an ambient atmosphere as follows; 157 mg (0.86 mmol) of $Zn(OAc)_2$ were dissolved in 1 mL of 2-methoxyethanol containing 4% MEA by volume. The mixed solution was stirring at 50 °C for 1 h. This was the standard MEA–ZnO precursor solution. On the other hand, 92.3 mg (0.35 mmol) of $Zn(acac)_2$ were dissolved in 1 mL of 2-methoxyethanol containing 10.6% AA by volume to prepare the new ZnO precursor solution, then the solution was filtered after stirring overnight at 50 °C. This mixed solution was the AA–ZnO precursor solution, using three equivalents of AA to $Zn(acac)_2$ to obtain an optimal concentration of $Zn(acac)_2$. Both precursor solutions were spin-coated onto the glass–ITO and PET–ITO substrates. The precursor films were heated at 100 °C or 250 °C for

1 h on a hot plate, to remove the solvent and the complexing agent. The ZnO films prepared from the conventional MEA–ZnO precursor solution and the novel AA–ZnO precursor solution were labeled as MEA–ZnO and AA–ZnO, respectively.

2.3. Fabrication of organic solar cells

The glass–ITO electrodes were cleaned by sonication in 2-propanol, washed in boiling 2-propanol, and then dried in air. PET–ITO electrodes were cleaned only by sonication in 2-propanol to prevent substrate warping. For spin-coating onto the flexible PET–ITO, the substrates were fixed onto glass plates using an adhesive thermal release sheet named "REVALPHA 3195" purchased from Nitto Denko Corp. The flowchart of the cell fabrication is shown in Fig. 2. The fabrication was carried out in air, controlling the relative humidity at less than 35%. The MEA–ZnO and AA–ZnO films were prepared by the method described above. A mixed CB solution of P3HT and PCBM (weight ratio = 5:4) was spin-coated onto the ITO/ZnO. A PEDOT:PSS dispersion in water containing 0.5 wt.% Triton-X 100 was spin-coated onto the PCBM:P3HT layer. The Au back electrode was vacuum deposited at 2×10^{-5} torr onto the PEDOT:PSS layer. Finally, the cell was heated at 150 °C for 20 s to remove it from the adhesive sheet. The effective area of the solar cell was restricted to 1 cm^2 by depositing the Au electrode with a shadow mask.

2.4. Measurements

The *I–V* curves of solar cells were measured by linear sweep voltammetry at a scan rate of 5 V min^{-1}, under AM 1.5G simulated sunlight irradiation at an intensity of 100 mW cm^{-2} (1 sun). Durability test of the solar cells was carried out by an interval LSV measurement in combination with a rest voltage measurement under continuous irradiation of the AM1.5-100 mW cm^{-2} light, according to the ISOS-protocols (ISOS-L-1) [23]. The light source was a SAN-EI Electric XES-502S solar simulator calibrated with an EKO MS-601 pyranometer. All electric measurements were performed using a Hokuto Denko HZ-5000 electrochemical analyzer. The X-ray diffraction (XRD) measurements were carried out using an X-ray diffractometer (Rigaku RINT 2500) with Cu Kα radiation at 40 kV × 200 mA. Atomic force microscopy (AFM) was carried out using a SII SPI3800N AFM apparatus. All measurements were carried out under an ambient atmosphere (ca. 25 °C/40–60%RH).

3. Results and discussion

The XRD patterns of the MEA–ZnO and AA–ZnO films did not show any peaks for crystalline ZnO, indicating that the ZnO in the film is amorphous. However, for both films heated at more than 350 °C, the XRD pattern exhibited three peaks, at $2\theta = 31.7°$, $2\theta = 34.4°$ and $2\theta = 36.2°$, labeled as orientations along the (100), (002) and (101) planes, respectively. In addition, each peak-intensity was nearly equal in AA–ZnO; in contrast, the peak of the (002) plane
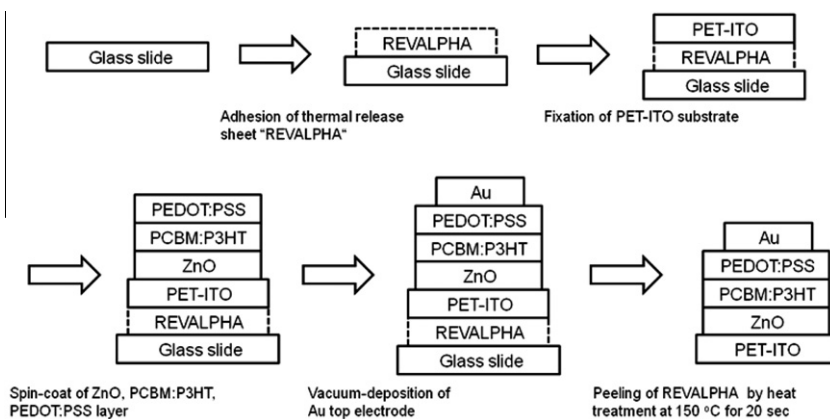
Fig. 2. Fabrication flowcharts of the flexible inverted polymer solar cells on PET substrate.

was very high in intensity compared with those of the (1 0 0) and (1 0 1) planes in MEA–ZnO. These results suggest that the novel AA–ZnO film has different features with respect to crystallinity and surface polarity.

Fig. 3 shows the surface AFM images of the sol–gel ZnO films on glass and PET substrates. Using the conventional MEA–ZnO precursor film on the glass–ITO, heated at 250 °C, the substrate was uniformly covered with ZnO particles as shown in Fig. 3a. However, the MEA–ZnO precursor film on the PET–ITO, heated at 100 °C, gave a poorly uniform ZnO cover as shown in Fig. 3b, which reveals height differences of more than 100 nm. These results suggest that the film morphology is changed dramatically by the rate of the solvent evaporation. Fig. 3c shows the surface AFM image of the AA–ZnO film on PET–ITO. The height difference of the AA–ZnO film was below 40 nm, and the ZnO nanoparticles, of about 400 nm in diameter, uniformly covered the PET–ITO despite the low-temperature process. AA could be more easily removed from the ZnO precursor film by heat treatment at 100 °C than MEA, since the boiling point of AA is much lower.

Fig. 4a shows the photo I–V curves of the inverted polymer solar cells fabricated on glass and PET substrates with

MEA–ZnO, and their performances are summarized in Table 1. When the conventional precursor film on the glass–ITO was heated at 250 °C, the MEA–ZnO cell had a short-circuit current (J_{sc}) of 7.45 mA cm^{-2}, open-circuit voltage (V_{oc}) of 0.55 V, fill factor (FF) of 0.55, and a PCE of 2.26%. In contrast, when the precursor films on the glass–ITO and PET–ITO were dried at 100 °C, the performances of the glass and the flexible MEA–ZnO cells were poorly reproducible. This was because the P3HT:PCBM layer only partially covered the rough ZnO surface. When a smooth surface was obtained by chance, the glass and PET devices had a J_{sc} of 6.57 mA cm^{-2}, V_{oc} of 0.55 V, FF of 0.53, and a PCE of 1.93%, and J_{sc} of 6.85 mA cm^{-2}, V_{oc} of 0.54 V, FF of 0.44, and a PCE of 1.65%, respectively. Fig. 4b shows the photo I–V curves of the inverted polymer solar cells on the glass and PET substrates covered with the AA–ZnO films, and the performances are also summarized in Table 1. When an AA–ZnO film heated at 250 °C on the glass was used, the cells showed relatively high performance with a J_{sc} = 8.10 mA cm^{-2}, V_{oc} = 0.55 V, FF = 0.58, and PCE = 2.56%. This result shows that the AA–ZnO film acts more effectively as the electron collection layer for the inverted polymer solar cell than the MEA–ZnO film. In
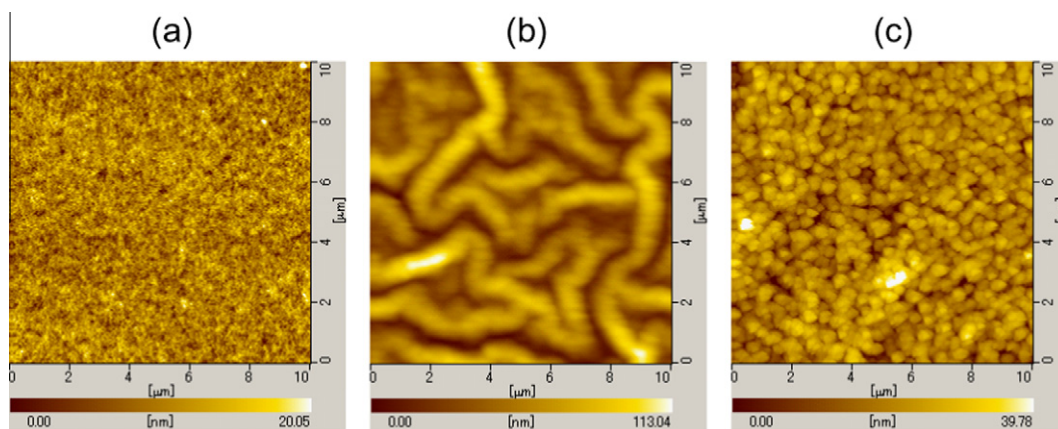

Fig. 3. Surface AFM images of the sol–gel ZnO films on glass or PET substrate prepared by various heat treatments; (a) MEA–ZnO, 250 °C, glass, (b) MEA–ZnO, 100 °C, PET and (c) AA–ZnO, 100 °C, PET.
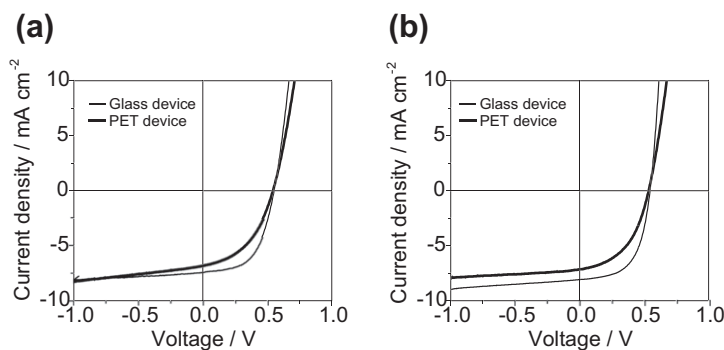
(a) **(b)**

Fig. 4. Photo *I–V* curves of the inverted polymer solar cells on glass or PET substrate with MEA–ZnO (a) or AA–ZnO layer (b) as electron collection layer. Heat treatment of ZnO film for the glass device was at 250 °C and for the PET device at 100 °C.

Table 1
Performance on Glass–ITO or PET–ITO with MEA–ZnO or AA–ZnO layer. The PCBM:P3HT film was prepared from the CB solution.

Substrate	ZnO	$T_{(ZnO)}$[a]/°C	$T_{(PCBM:P3HT)}$[b]/°C	J_{sc}/mA cm^{-2}	V_{oc}/V	FF	PCE/%
Glass–ITO	MEA–ZnO	250	150	7.45	0.55	0.55	2.26
Glass–ITO	MEA–ZnO	100	150	6.57	0.55	0.53	1.93
PET–ITO	MEA–ZnO	100	Room temp.	6.85	0.54	0.44	1.65
Glass–ITO	AA–ZnO	250	150	8.10	0.55	0.58	2.56
Glass–ITO	AA–ZnO	100	Room temp.	7.31	0.56	0.57	2.33
PET–ITO (ave.)	AA–ZnO	100	Room temp.	6.93	0.56	0.48	1.84
PET–ITO (max.)	AA–ZnO	100	Room temp.	7.33	0.55	0.53	2.15

[a] Drying temperature of ZnO.
[b] Heating temperature of PCBM:P3HT.

addition, the performance of the flexible AA–ZnO cell was highly reproducible even when the novel precursor film on the PET was dried at only 100 °C. The average PCE value of 1.84% was obtained for the flexible AA–ZnO cells although the best PCE was 2.15%. Moreover, the glass AA–ZnO cells showed 2.33% of PCE.

To improve the performance of the flexible cell, a small amount of NB was added to the CB solution of P3HT:PCBM, being denoted the CB:NB solvent. Though NB was a poor solvent for P3HT and PCBM, it was known that its addition improves the crystallinity and the thermal stability of P3HT and PCBM in a solid film [24]. Fig. 5 shows the PCE against NB vol.% for the flexible cells containing PCBM:P3HT blend film prepared using the CB:NB solvent. The value increased with increasing additive. When the blend film was prepared using CB containing 2 vol.% NB, the improved performance of J_{sc} = 7.33 mA cm^{-2}, V_{oc} = 0.57 V, FF = 0.62, and PCE = 2.62% was obtained. However, its durability was relatively low, for example, the PCE dropped to 1.56% after irradiation with 1 sun for 100 h. On the other hand, when the PCBM:P3HT film was prepared using only CB solvent, the PCE of the non-sealed flexible AA–ZnO cell maintained 96% of the maximum value (PCE = 1.81%), see Fig. 6. High stability was demonstrated for the non-sealing AA–ZnO cell.
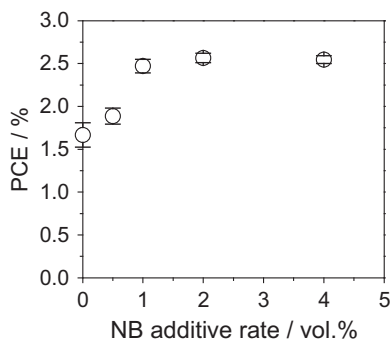

Fig. 5. Plots of PCE of the flexible inverted polymer solar cells containing PCBM:P3HT blend film prepared using CB:NB solvent, against vol.% of NB added.
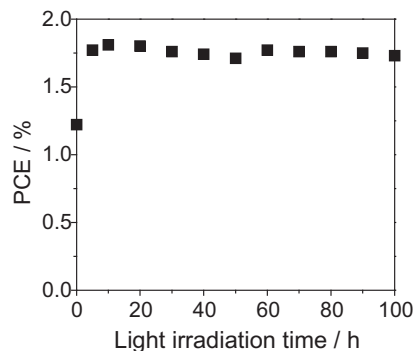

Fig. 6. Irradiation time dependence of the PCE for the non-sealed flexible AA–ZnO cell in air. The PCBM:P3HT blend film was prepared using the CB solution.

4. Conclusions

When the novel precursor solution containing $Zn(acac)_2$ and AA was used, the AA–ZnO film functioned sufficiently well as an electron collection layer even with a low-temperature process such as drying at 100 °C. Thus, we have easily fabricated a flexible PET–ITO/ZnO/PCBM:P3HT/PEDOT:PSS/Au cell without warping of the thin PET film. The maximum PCE was 2.15% for the non-sealed device with 1 cm^2 of effective area in air. In addition, these air stable cells maintained a relative efficiency of over 95% under continuous irradiation for 100 h.

Acknowledgments

References

[1] B. Kippelen, J.-L. Bredas, Energy Environ. Sci. 2 (2009) 251–261.
[2] J. Peet, A.J. Heeger, G.C. Bazan, Acc. Chem. Res. 42 (2009) 1700–1708.
[3] M. Helgesen, R. Sondergaard, F.C. Krebs, J. Mater. Chem. 20 (2010) 36–60.
[4] A.W. Hains, Z. Liang, M.A. Woodhouse, B.A. Gregg, Chem. Rev. 110 (2010) 6689–6735.
[5] S.H. Park, A. Roy, S. Beaupre, S. Cho, N. Coates, J.S. Moon, D. Moses, M. Leclerc, K. Lee, A.J. Heeger, Nat. Photon. 3 (2009) 297–302.
[6] H.-Y. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu, G. Li, Nat. Photon. 3 (2009) 649–653.
[7] C.-H. Hsieh, Y.-J. Cheng, P.-J. Li, C.-H. Chen, M. Dubosc, R.-M. Liang, C.-S. Hsu, J. Am. Chem. Soc. 132 (2010) 4887–4893.
[8] Y. Liang, Z. Xu, J. Xia, S.T. Tsai, Y. Wu, G. Li, C. Ray, L. Yu, Adv. Mater. 22 (2010) E135–E138.
[9] G. Zhao, Y. He, Y. Li, Adv. Mater. 22 (2010) 4355–4358.
[10] Y.-J. Cheng, C.-H. Hsieh, Y. He, C.-S. Hsu, Y. Li, J. Am. Chem. Soc. 132 (2010) 17381–17383.
[11] S.A. Gevorgyan, M. Jørgensen, F.C. Krebs, K.O. Sylvester-Hvid, Sol. Energy Mater. Sol. Cells 95 (2011) 1389–1397.
[12] M. Jørgensen, K. Norrman, S.A. Gevorgyan, T. Tromholt, B. Andreasen, F.C. Krebs, Adv. Mater. 24 (2012) 580–612.
[13] T. Kuwabara, T. Nakayama, K. Uozumi, T. Yamaguchi, K. Takahashi, Sol. Energy Mater. Sol. Cells 92 (2008) 1476–1482.
[14] T. Kuwabara, H. Sugiyama, T. Yamaguchi, K. Takahashi, Thin Solid Films 517 (2009) 3766–3769.
[15] T. Kuwabara, H. Sugiyama, M. Kuzuba, T. Yamaguchi, K. Takahashi, Org. Electron. 11 (2010) 1136–1140.
[16] T. Kuwabara, Y. Kawahara, T. Yamaguchi, K. Takahashi, ACS Appl. Mater. Interfaces 1 (2009) 2107–2110.
[17] T. Kuwabara, M. Nakamoto, Y. Kawahara, T. Yamaguchi, K. Takahashi, J. Appl. Phys. 105 (2009) 124513.
[18] I. Sasajima, S. Uesaka, T. Kuwabara, T. Yamaguchi, K. Takahashi, Org. Electron. 12 (2011) 113–118.
[19] F.C. Krebs, Sol. Energy Mater. Sol. Cells 92 (2008) 715–726.
[20] F.C. Krebs, Y. Thomann, R. Thomann, J.W. Andreasen, Nanotechnology 19 (2008) 424013.
[21] F.C. Krebs, Org. Electron. 10 (2009) 761–768.
[22] F.C. Krebs, S.A. Gevorgyan, J. Alstrup, J. Mater. Chem. 19 (2009) 5442–5451.
[23] M.O. Reese, S.A. Gevorgyan, M. Jørgensen, E. Bundgaard, S.R. Kurtz, D.S. Ginley, D.C. Olson, M.T. Lloyd, P. Morvillo, E.A. Katz, A. Elschner, O. Haillant, T.R. Currier, V. Shrotriya, M. Hermenau, M. Riede, K.R. Kirov, G. Trimmel, T. Rath, O. Inganäs, F. Zhang, M. Andersson, K. Tvingstedt, M. Lira-Cantu, D. Laird, C. McGuiness, S. Gowrisanker, M. Pannone, M. Xiao, J. Hauch, R. Steim, D.M. DeLongchamp, R. Rösch, H. Hoppe, N. Espinosa, A. Urbina, G. Yaman-Uzunoglu, J.-B. Bonekamp, A.J.J.M. van Breemen, C. Girotto, E. Voroshazi, F.C. Krebs, Sol. Energy Mater. Sol. Cells 95 (2011) 1253–1267.
[24] L. Chang, H.W.A. Lademann, J.-B. Bonekamp, K. Meerholz, A.J. Moulé, Adv. Funct. Mater. 21 (2011) 1779–1787.