



Polymer solar cell by blade coating

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ABSTRACT

Polymer bulk hetero-junction solar cells of poly(3-hexylthiophene) (P3HT) donor and (6,6)-phenyl-C61-butyric acid methyl ester (PCBM) acceptor are fabricated by blade coating in toluene solution. Desired donor–acceptor self-organization is achieved without the slow drying process and high boiling point solvent. Power conversion efficiency is 3.8%, much higher than the 2.6% obtained by spin coating in toluene solution. The blade coating method has nearly 100% material usage and can be integrated in the roll-to-roll process with high throughput production.

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Recently conjugated polymer solar cells have attracted great interests due to their unique properties such as easy solution process for large-area, light weight, and mechanical flexibility. The polymer bulk hetero-junction cells have interpenetrating networks of electron donors and acceptors, resulting in an efficient exciton dissociation and high photo-currents with the power conversion efficiency (PCE) about 5% [1,2]. Although the efficiency is not as high as that of inorganic solar cells, the potential of low-cost and roll-to-roll process on flexible substrates makes the polymer solar cells attractive as the solution to the serious energy challenges. However, to date most of the efficient polymer solar cells are made by spin coating, which causes serious material waste and raises the cost dramatically. In addition, the spin coating process is not easy to scale up to very

large sizes up to meters and is incompatible with the roll-to-roll process for high throughput production. Furthermore one major problem of the spin coated polymer solar cell is that a very toxic high boiling point organic solvent like dichlorobenzene (180.5 °C) or chlorobenzene (131 °C) is necessary for high efficiency. The high boiling point allows a slow drying process where the donor and acceptor molecules self-assemble into an interpenetrating network [1]. The high toxicity of dichlorobenzene and chlorobenzene makes the mass production environmentally unfriendly, and the slow drying process delays the production throughput. Although there have been researches on fabrication processes, including ink-jet printing [3], screen printing [4], spray coating [5], and blade coating [6], the development of alternative solution coating methods compatible with the low-cost and environmentally friendly mass production remains a crucial problem [7]. Since there is no necessary for organic layers to be

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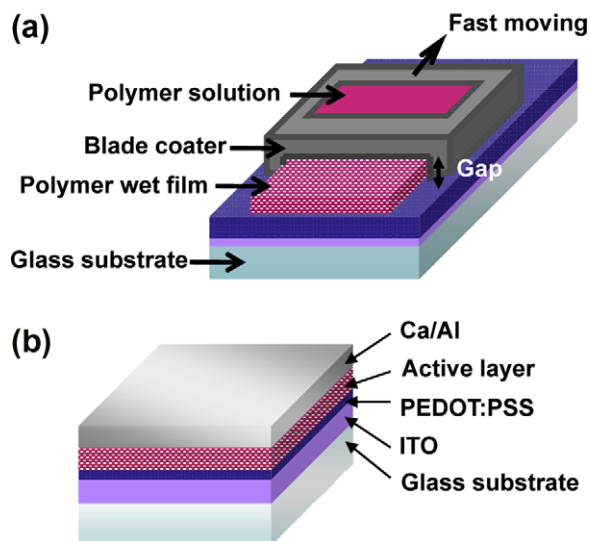


Fig. 1. (a) Schematic working principle of blade coating. The polymer wet film is formed by moving the blade coater. The thickness of polymer wet film is defined by the gap of the blade coater. (b) The schematic device structure of the bulk hetero-junction cells.

structured by printing in organic solar cells, blade coating for large area fabrication has been proved to be the better way [6]. The film thickness by blade coating can be reduced to nanometer scale by carefully controlling the fabrication parameters such as the solution concentration, the blade gap, and the blade coating speed. Recently we verified the feasibility of blade coating for high-efficiency polymer light-emitting diodes [8]. Unlike spin coating, the area can be easily scaled up and the material usage is almost 100% in blade coating. In this work, blade coating is applied to poly(3-hexylthiophene) (P3HT) and (6,6)-phenyl-C61-butyric acid methyl ester (PCBM) blend in the toluene solution which has a lower boiling point (110 °C) and is less toxic. High efficiency is achieved from toluene solution without the slow solvent evaporation process.

Fig. 1a shows the schematic working principle of blade coating. The thickness of the wet polymer film is defined by the gap. The polymer dry film thickness is tuned by the polymer concentration in solution and the gap of the blade coater. The polymer wet film is deposited by dragging the blade coater at a certain speed about 15 cm/s. We first focus on solar cells with P3HT:PCBM blend dissolved in toluene. Device performances are compared for

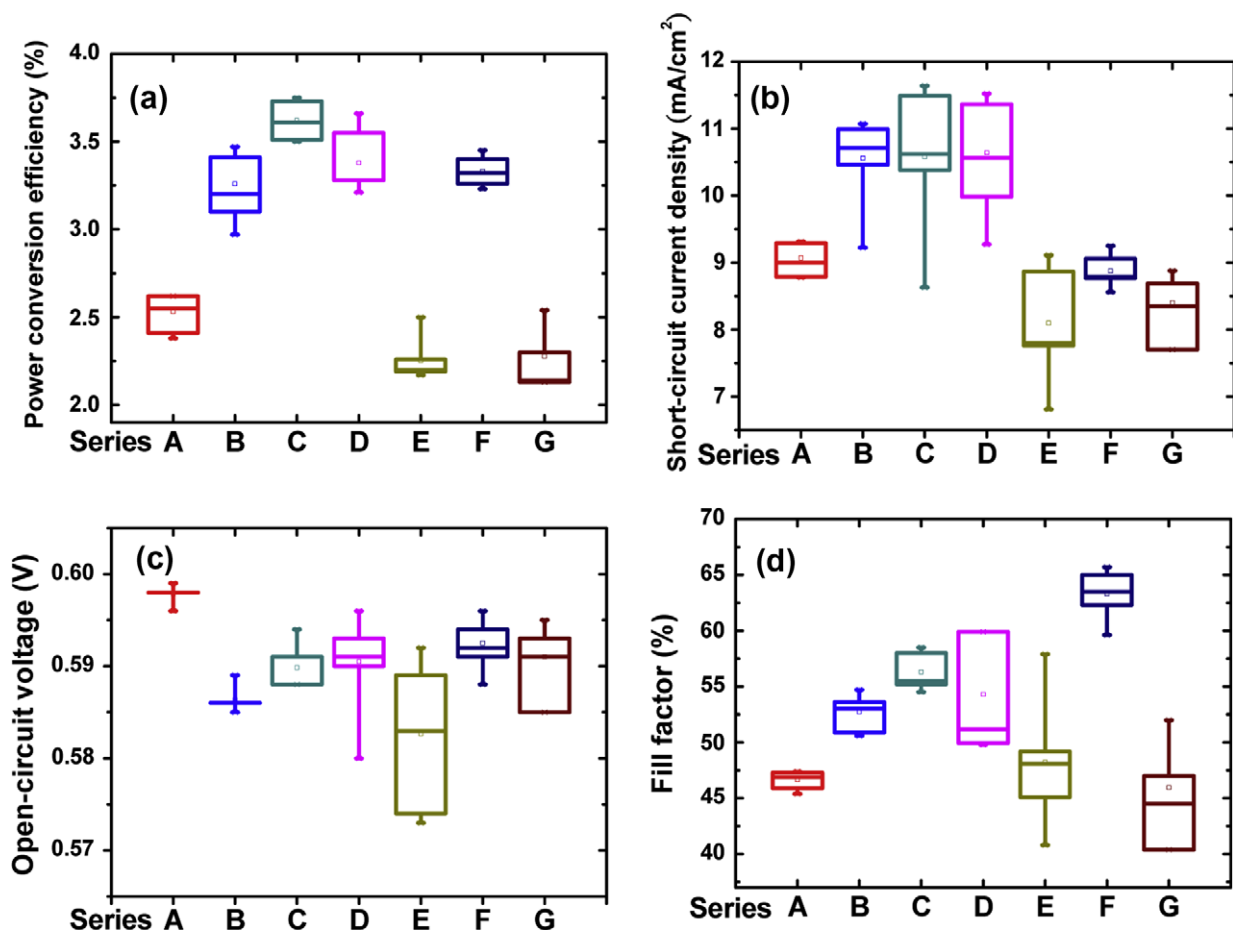


Fig. 2. Statistical results of the seven series of devices: (a) the power conversion efficiency, (b) the short-circuit current, (c) the open-circuit voltage and (d) the fill factor. The horizontal lines in the box denote the 25th, 50th, and 75th percentile values. The error bars denote the 5th and 95th percentile values. The open square inside the box denotes the mean value.

different coating methods including spin coating, blade coating, blade coating on a hot plate, as well as blade and spin coating. For the blade and spin coating the polymer wet film is deposited by blade coating which is followed by spinning until the dry film is formed. In all cases the weight ratio of P3HT and PCBM is 1:1. The device structure is ITO/PEDOT:PSS/P3HT:PCBM/Ca/Al shown in Fig. 1b. ITO is indium tin oxide and PEDOT:PSS is poly-(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (Baytron PVP Al 4083). A 40 nm PEDOT:PSS layer is spin coated on a patterned ITO substrate and baked at 200 °C in nitrogen for 15 min.

Seven series of devices with six devices in each are made to study the different coating processes with different solvents statistically. Among them, five series are made with toluene solution to compare the coating processes, including spin coating (series A), blade coating (series B), blade coating on a hot plate at 60 °C (series C), as well as blade and spin coating (series D). In addition, the devices with the PEDOT:PSS layer by blade coating at 100 °C and P3HT:PCBM by blade and spin coating from toluene solution is made to study the feasibility of bladed PEDOT:PSS layer (series G). The other two series made from two conventional high boiling point solvents, chlorobenzene (series E) and dichlorobenzene (series F), are compared with those from toluene by blade and spin coating. After coating all the P3HT:PCBM layers are annealed at 140 °C for 20 min in nitrogen. The Ca(35 nm)/Al(100 nm) cathode is deposited by thermal evaporation. The active area of the device is 0.04 cm². All the devices are packaged in the glove box and measured in the ambient environment. The power conversion efficiency is measured by the solar simulator (PEC-L11, Peccell Technologies) under AM1.5G irradiation. The incident photon-to-electron conversion efficiency (IPCE) is measured by the spectral response measurement system (SR300, Optosolar GMBH). The morphology of P3HT:PCBM is monitored by atomic force microscope (AFM, Dimension 3100, Digital Instruments).

Fig. 2 shows the statistical results of the seven series of devices. Among the series based on toluene solution (series A, B, C, D, and G), the series of devices by blade coating have the higher efficiencies except the series with bladed the PEDOT:PSS layer. Because the open-circuit voltages V_{oc} are about the same, the high performances of series B, C, and D result from the high short-circuit currents J_{sc} and fill factor. Among the series by blade and spin coating (series D, E, and F), the series of devices from toluene solution and dichlorobenzene have the higher performances. While the J_{sc} of series E and series F are about the same, the high performance of series F results from the relatively high fill factor. For further discussion, the best devices in each series are chosen to show the advanced device properties.

Fig. 3a shows the current–voltage (J – V) curves of five devices in toluene solution made by different active layer coating processes. The short-circuit currents J_{sc} made by blade coating (device B, C, and D) are larger than that of the device made by conventional spin coating (device A). Using blade coating the J_{sc} increases from 9.3 mA/cm² with spin coating to 11.5 mA/cm². The fill factor rises from 47% to 55% and the open-circuit voltage V_{oc} remains the same. The efficiency, which is proportional to J_{sc} , V_{oc} , and fill fac-

tor as a whole, is improved from 2.6% (device A) by spin coating to 3.8% (device C) by blade coating on a hot plate.

It is believed that in order to get a high efficiency in bulk hetero-junction polymer solar cell the microscopic morphology of the active layer needs to be well controlled to achieve an ordered structure by certain annealing processes such as slow solvent evaporation [1] and postproduction heat treatment [2,9]. Such annealing promotes molecular self-organization and makes the polymer chains more ordered in its domains. In spin coating for low boiling point solvents such as toluene (110 °C), high volatility leads to the fast drying of the active layer and may limit the self-assembly as well as the power conversion efficiency. However, the polymer films made by blade coating could be more ordered than those by spin coating due to the fact that the polymer chains are relatively free to move in the absence of centrifugal force. Therefore even without the slow drying process the donors and acceptors quickly

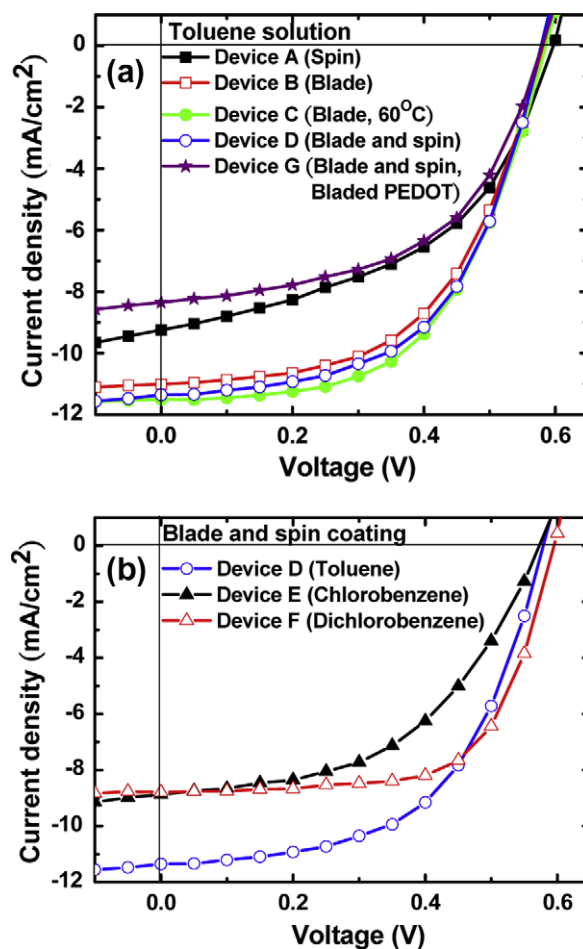


Fig. 3. Current–voltage (J – V) relations of the devices in this work. (a) Devices made by spin coating (device A, solid square), blade coating (device B, empty square), blade coating at 60 °C (device C, solid circle), and blade and spin coating (device D, empty circle) in toluene solution, blade and spin coating with bladed PEDOT:PSS (device G, solid star). (b) Devices made by blade and spin coating in toluene solution (device D, empty circle), chlorobenzene solution (device E, solid triangle), and dichlorobenzene solution (device F, empty triangle).

Table 1

Performance of bulk hetero-junction solar cells in this work.

Label	J_{sc} (mA/cm ²)	V_{oc} (V)	Fill factor (%)	PCE (%)	Thickness (nm)
A. (Toluene) spin	9.25	0.59	47	2.6	223
B. (Toluene) blade	11.07	0.59	53	3.5	412
C. (Toluene) blade at 60 °C	11.49	0.59	55	3.8	304
D. (Toluene) blade and spin	11.36	0.58	55	3.7	245
E. (Chlorobenzene) blade and spin	8.87	0.57	49	2.5	345
F. (Dichlorobenzene) blade and spin	8.79	0.60	66	3.5	242
G. (Toluene) blade and spin with bladed PEDOT:PSS (120 nm)	8.35	0.59	52	2.5	245

self-assemble into the desired ordered and interpenetrating morphology during the blade coating process. We speculate that the quick assembly occurs at the beginning of the blade coating because the device made by blade and spin coating (device D) shows high efficiency as well. Interestingly, device B, C, and D have different film thickness but similar performances. High efficiency is maintained for device B with 412 nm thickness probably because pure

blade coating with neither heating nor spinning give the highest freedom to chain motions and the most ordered morphology. In short, the blade coating method allows an ordered polymer morphology in a fast drying solution like toluene. In addition, the result of the device with the bladed PEDOT:PSS and blade and spin coated P3HT:PCBM layer is also shown in Fig. 3a. The efficiency of device G is 2.5% with J_{sc} of 8.35 mA/cm², V_{oc} of 0.59 V, and fill factor

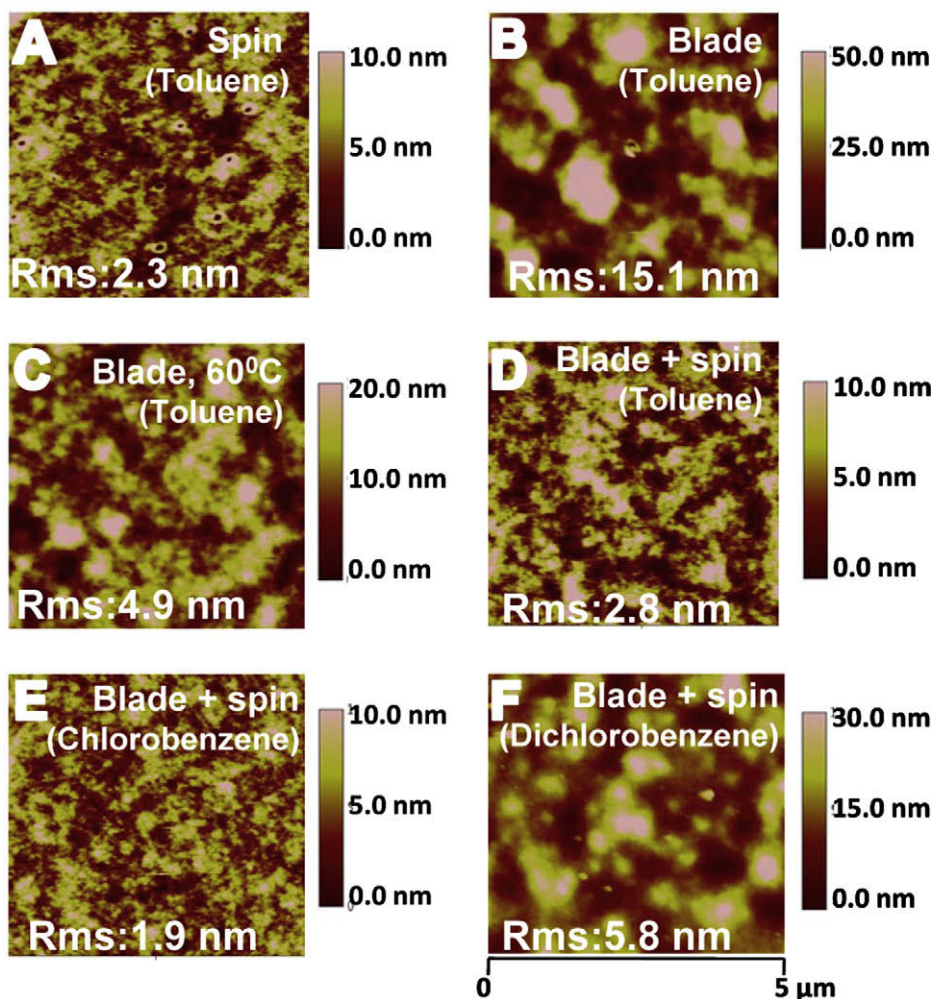


Fig. 4. AFM images of the devices in this work. P3HT:PCBM thin film made by: (a) spin coating, (b) blade coating, (c) blade coating at 60 °C, (d) blade and spin coating and (e) blade and spin coating in chlorobenzene solution, (f) blade and spin coating in dichlorobenzene solution. The P3HT:PCBM films in (a)–(d) are made in toluene solution.

of 52%. The relative low performance of device G results from the thick PEDOT:PSS film (120 nm), which causes high series resistance. It is difficult for us to reduce the PEDOT:PSS film thickness now because we use the PEDOT:PSS solution from H. C. Stark without any further dilution. The concentration needs to be lowered without sacrificing the conductivity to get the normal film thickness (40 nm). More experiments need to be done to optimize the PEDOT:PSS layers by blade coating. Nevertheless, such device shows the feasibility of all blade coated devices with very low cost and high throughput in mass production.

Now we turn to different solvent systems. Two devices are made by conventional high boiling points solvents chlorobenzene (device E) and dichlorobenzene (device F). Fig. 3b shows the results of the devices by the fast-drying blade and spin process with different solvents. There is no slow solvent evaporation in the fabrication process. The power conversion efficiencies are 2.5% in the device from chlorobenzene solution (device E) and 3.5% in that

from dichlorobenzene solution (device F). The J_{sc} are both about 8.8 mA/cm², which is significantly smaller than J_{sc} of 11.4 mA/cm² in device D from toluene. Interestingly high boiling point solvents give higher J_{sc} for spin coating but smaller J_{sc} for blade coating. There are probably more P3HT/PCBM interfaces in toluene solution than those in chlorobenzene and dichlorobenzene solutions, resulting in more efficient exciton dissociation. It is remarkable that the fill factor of dichlorobenzene solution is 66%, much higher than 55% for toluene and 49% for chlorobenzene. Dichlorobenzene has the highest boiling point among the three solvents. The highest fill factor in dichlorobenzene solution may result from the highest carrier mobility due to the enhanced self-assembly of P3HT taking place during the relatively slow drying in spinning. The device performances are summarized in Table 1.

The AFM images of the devices are shown in Fig. 4. The root-mean-square roughness are 2.3 nm for device A, 15.1 nm for device B, 4.9 nm for device C, 2.8 nm for device D, 1.9 nm for device E, and 5.8 nm for device F. The different root-mean-square values are attributed to the different fabrication processes with different solvents. Neat P3HT layers by any process would be very rough (15 ± 3 nm) due to the fact that the polymer chains have the trend to form crystallization, and the neat PCBM could not even form thick films by blade coating. We think that the devices with high efficiency (device B, C, D, and F) have stronger self-organization than those with low efficiency (device A and E). Higher surface roughness corresponds to higher degree of self-organization. [10,11] However, there is no clear evidence for the correlation between self-organization and device efficiency. Nevertheless, we speculate that device B by blade coating shows clear self-organization, implying ordered structures within each component. Therefore, the carrier mobility is high and the power conversion efficiency is high as well even with a thick film of 412 nm. The clear self-organizations in device C and device F also could be seen due to their relative high roughness. Interestingly, the roughness of device D by blade and spin coating is just slightly higher than that of device A only by spin coating, but the efficiency of device D is still much higher. This may be due to the ordered structure occurred at the beginning of blade coating, combined with thicker film thickness by blade coating. As for the low efficiency devices such as device A and device E, the films are relatively smooth. The images show that the self-organization could be achieved within the short drying time by blade coating.

Fig. 5a shows the absorption spectra of the P3HT and PCBM blend films deposited by different methods and solutions. The IPCE for all devices are shown in Fig. 5b. Despite of the different morphologies there is no significant variations among the absorption spectra. So the differences in the device performances must come from the exciton dissociation and carrier transport processes. The IPCE values appear similar in all the devices except that of device G and show slightly difference at about 600 nm. However, the J_{sc} values show much difference among the devices. In principle the measured J_{sc} should be proportional to the product of the IPCE and the illuminating spectrum, integrated over all wavelengths. We may attribute the incon-

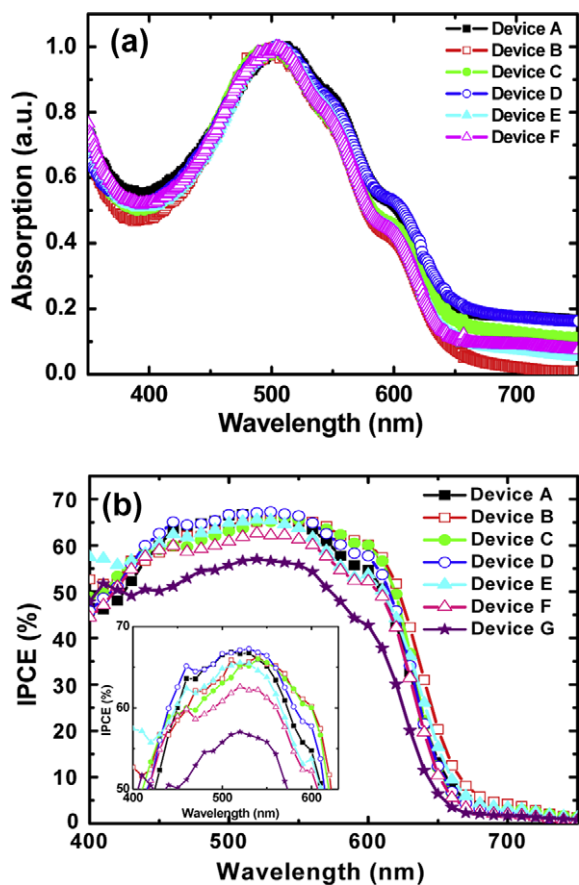


Fig. 5. (a) The absorption spectra of the devices and (b) the incident photon to current efficiency (IPCE) in this work. The inset shows the IPCE from 400 nm to 600 nm for clarity. Devices made by spin coating (device A, solid square), blade coating (device B, empty square), blade coating at 60 °C (device C, solid circle), and blade and spin coating (device D, empty circle) in toluene solution. Devices made by blade and spin coating in chlorobenzene solution (device E, solid triangle), and in dichlorobenzene solution (device F, empty triangle), as well as blade and spin coating with bladed PEDOT:PSS (device G, solid star).

sistency between IPCE and J_{sc} values to the different spectral-mismatch factors of the different light sources.[6]

In conclusion we develop the blade coating method to fabricate bulk hetero-junction polymer solar cells with decent power conversion efficiency of 3.8%. The active layer is deposited in toluene solution, which is less toxic than the conventional chlorobenzene and dichlorobenzene solution optimized for spin coating. In sharp contrast to spin coating there is almost no material waste in blade coating. Moreover, this method can be easily scaled up to large sizes as meters and can be applied in a future roll-to-roll fashion for high volume production.

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