Co-solvents roles in PEDOT:PSS ink-jet inks

Atasheh Soleimani-Gorgani

Department of Printing Science and Technology, Institute for Color Science and Technology, PO Box 16765654, Tehran, Iran

E-mail: asoleimani@icrc.ac.ir

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Abstract
The different water soluble ink-jet inks based on conjugated poly (3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) were formulated with various organic co-solvents such as diethylene glycol (DEG), triethylene glycol (TRIEG), tetraethylene glycol (Tetra EG), and polyethylene glycol (PEG) to print on the flexible substrate. The effect of adding various organic co-solvents, which show a same trend of molecular weight, dipole moment and boiling point on the formulated inks properties and ink-jet printed films electrical conductivity, morphology and transparency were investigated. The conductivities of the ink-jet printed films were evaluated by four-point probe conductivity measurement. The morphologies of the printed films have been studied using atomic force microscopy and scanning electron microscopy. The size of PEDOT:PSS particles and the printed film morphology altered by addition of different types of co-solvent in the ink-jet ink formulation. The electrical conductivity of the ink-jet printed film increased by raising the molecular weight, boiling point and dipole moment of used co-solvent in ink-jet ink formulation.

Keywords: ink-jet printing, conductivity, PEDOT:PSS, conductive polymer

Classification numbers: 4.10, 5.10, 6.00

1. Introduction

Polymeric materials, especially conducting polymers [1–5] are a promising candidate for application in various flexible optoelectronic devices such as light-emitting diodes, field effect transistors, and organic solar cells that are based on charge transport properties of the comprised materials.

The amorphous materials such as polymers due to their electronic, optical and mechanical properties and their ability for a low cost of device fabrication for instance solution process [6, 7] have been used instead of crystalline, brittle and expensive indium tin oxide (ITO) [8, 9], carbon nanotubes [10–12], graphene [13–16], metal nanowires [17–19], metal grids [20] and thin metals [21]. The solution process allows for the elimination of high vacuum and temperature processes such as vacuum evaporation, sputtering [2, 5] and the use of flexible substrates to produce flexible devices [22, 23]. Among a number of conducting polymers, an aqua dispersion of poly (3,4-ethylenedioxythiophene) (PEDOT) is the material most widely used in optoelectronic devices. One of the more common uses of PEDOT:PSS is in an antistatic layer in photographic films (AGFA-Gevaert NV) that need highly conductivity, whereas low conductivities are appropriate for the wide-spread use as a transparent anode electrode in flexible electronic devices or a hole-transport layer in organic light emitting diodes, conductivities in the range of $10^{-3}$ S·cm$^{-1}$.

In the PEDOT:PSS, the PEDOT is a conductive p-type polymer that is not soluble in polar solvents such as water. Therefore, it doped with PSS, which is an ionic conductor to provide a stable, easy-to-process, deep blue water-based PEDOT:PSS dispersion [24]. The PSS in the complex functions as a counter ion for the cationic, conductive PEDOT. Although the addition of PSS brings an enhanced process-ability, this comes at the expense of a decreased electrical conductivity. A structural model of PEDOT:PSS is shown in figure 1. In this model, oligomer PEDOT segments are tightly, by ion interaction bond attached to PSS chains of much higher molecular weight and that coils up to form a tertiary structure [25–27]. The high conductivity of PEDOT:PSS dispersions can then be attributed to set arrangements of the PEDOT chains within a larger, tangled structure of loosely
cross-linked, highly water-soluble PSS particles. The PEDOT:PSS can easily be fabricated by solution processes such as spin coating, dip coating, ink-jet printing and conventional printing to produce a thin, optically transparent, conductive films. In this study, the drop-on-demand (DOD) ink-jet printing that has grown to a major topic in scientific research due to their low price, low space demand, environmental safety, minimum chemical waste and ability to print any image or pattern from monitor on the desired location onto various substrates was chosen. Ink-jet printing is a non-contact method in which desired amount of ink droplets are directly deposited from very fine nozzles through a computer designed image onto a selected area of a substrate without any contamination. The two most popular types of DOD ink-jet printers are thermal and piezoelectric. Compared to conventional manufacturing method ink-jet printing can be carried out in low temperatures. Despite all the advantages of the ink-jet printing technology, nozzle clogging and achieving a uniform printed film has always been a major problem. The nozzle clogging occurs when the ink-jet printing inks contain insoluble micro or nanoparticles that can be agglomerated and precipitated during the printing process. The non-uniform printed film is due to either improper ink physical properties or drying time of printed film. Therefore, preparing the ink-jet ink is often a challenging issue for researchers.

Recently, various studies have demonstrated to enhance the conductivity of spin coated or sprayed PEDOT:PSS onto the glass or PET substrates by the post-treatments with acids [28, 29], changing the PEDOT:PSS ratios [30], treatment of PEDOT:PSS with polar organic solvents such as alcohols [31] or the addition of an ionic liquid [32], an anionic surfactant [33] or solvents such as dimethyl sulfoxide [30], sorbitol [34], diethylene glycol [35] or ethylene glycol [36] into the PEDOT:PSS aqueous solution. Adding co-solvents include dielectric screening due to the solvent, conformational changes of the PEDOT chain or morphological changes [35, 37–39].

In this study, the various organic co-solvents, which have different structures, dipole moments and boiling points are added to the ink formulation to not only adjust the physical properties of ink-jet ink to improve the wettability of the polymer on the substrate but also to optimum the drying times of ink-jet printed film to achieve optimum conductivity and transparency.

2. Experimental

2.1. Material
The materials used in this experiment were: poly (3,4-ethylene dioxythiophene): polystyrene sulfonate (PEDOT:PSS) as 1.3 wt% dispersion in H2O (1 S cm−1) and ITO coated polyethylene terephthalate (PET) with surface resistivity 60 Ω sq−1 were provided by Sigma-Aldrich; the various co-solvents such as diethylene glycol (DEG), triethylene glycol (TRIEG), tetraethylene glycol (TETRAEG), polyethylene glycol 200 (PEG200) and all other related substances used in this work were chosen from laboratory grade as received from Merck Company (Germany). Table 1 shows the properties of the co-solvents used in the PEDOT:PSS ink formulations.

$$\text{Table 1. The properties of co-solvents used in the formulations.}$$

| Ink | Name | Structure | Dipole moment (Debye) | Boiling point (°C) |
|-----|------|-----------|----------------------|-------------------|
| 1   | Diethylene glycol (DEG) | HO−O−OH | 2.7 | 245 |
| 2   | Triethylene glycol (TRIEG) | HO−O−O−OH | 2.99 | 288 |
| 3   | Tetraethylene glycol (TRIEG) | HO−O−O−O−OH | 3.25 | 329 |
| 4   | Polyethylene glycol (PEG) | H−O−O−O−H | 3.6 | >300 |

2.2. Equipment and instrumentation
The prepared ink formulations were filtered through a 0.45 μm and 0.2 μm Sartorius Minisart filter (Göttingen, Germany). The indium tin oxide coated PET were ink-jet printed using
an Epson Stylus Photo P50 printer in 1 and 3 printing runs.

Table 2. The PEDOT:PSS inks formulations (wt%).

| Ink composition | Ink1 | Ink2 | Ink3 | Ink4 |
|-----------------|------|------|------|------|
| PEDOT:PSS       | 5    | 5    | 5    | 5    |
| DE-ionized water| 10   | 10   | 10   | 10   |
| Isopropanol     | 2    | 2    | 2    | 2    |
| DEG             | 1    | —    | —    | —    |
| TRIEG           | —    | 1    | —    | —    |
| TETRAEG         | —    | —    | 1    | —    |
| PET             | —    | —    | —    | 1    |

Figure 2. Rheology behavior of PEDOT:PSS inkjet ink formulation at different shear rates.

3. Results and discussion

3.1. Rheological behavior

The viscosity of the prepared ink predominantly affects the rheological behaviors through the capillary nozzles of the printer. Figure 2 shows the variation of viscosities along with shear rates for the prepared water soluble inks on a logarithmic scale. It is apparent that the viscosity of the inks has remained almost unchanged by increasing the shear rate; demonstrating that the inks behave as a Newtonian fluid. Consequently, the type of co-solvents had no effect on rheological behavior of the PEDOT:PSS inks, and viscosity of the prepared inks was found to be in acceptable range at shear rate 1000 s\(^{-1}\) [42]. However, the viscosity of the prepare inks increased from 0.0014 to 0.002 Pa \(\cdot\) s at shear rate 1000 s\(^{-1}\) by increasing the molecular weight of adding co-solvents.

3.2. Surface tension

Surface tension of the prepared inks plays important roles not only in wettability of the ink onto the substrate but also in decomposition of the ink into fine drops through the capillary tubes of the printer nozzle. Water, as the most important phase in the ink formulation, played the primary role in controlling surface tension. Surface tension of the prepared inks (table 3)
A Soleimani-Gorgani was found to be in acceptable range 37.5 to 45 mN · m$^{-1}$ for commercial ink-jet inks [43].

### 3.3. DLS of PEDOT:PSS inks

The size of the PEDOT:PSS particles in the prepared inks (Ink1-Ink4) were determined by dynamic light scattering (DLS). DLS results presented in figure 3 indicates, the particle size of PEDOT:PSS for all the prepared ink are on the acceptable range to use in ink-jet printing process. The DLS results show that, as the size of molecular structure of co-solvent increased, the particle size of PEDOT:PSS increased. These results prove that the type of co-solvents effect to the morphology of PEDOT:PSS chain. The PEDOT:PSS has a tertiary structure with a diameter of several tens nanometer, where hydrophobic PEDOT molecules aggregate to form physical cross-links between the PSS chains in water. Adding organic co-solvents in ink formulation may bring a screening effect between the positively charged PEDOT chains and negatively charged PSS chains and then reducing the coulomb interaction between them, which causes a phase separation between PEDOT and PSS (figure 4). Therefore, by increasing the molecular size of co-solvent the space between the PEDOT and PSS chains increased that cause increasing in the PEDOT: PSS particle size.

### 3.4. Electrical properties

The conductivity of ten different locations on each ink-jet printed samples were measured and an average of the measured values were calculated and presented in table 4. The results in table 4 clearly show that the electrical of the PEDOT:PSS ink-jet printed depend noticeably on the types of co-solvents. An assessment of the conductivity values between the different co-solvents shows that the samples, which have higher dipole moment, boiling point, molecular weight as a co-solvent in the ink formulation have higher conductivity than the other samples. This is consistent with the difference in co-solvents formulated in ink-jet ink affects the printed film conductivity. In the PEDOT:PSS dispersion the polymer chains have shown in most occurrence to adapt a random coil conformation. A thin film is formed with grains containing of doped conjugated polymer coils, when the dispersion is printed onto a substrate [5, 6]. PSS chains are made up of several hundred monomer units, the polymer grains are distinguished by the PSS random coil with ionically attached PEDOT chains. In polar and protic solvents, which have large dipole moment and can donate proton (H$^+$) cause the removal of the negative charge PSS$^-$ chain ($SO_3^-$) to produce PSS-H$^+$ by effectively screening them from the positively charged hydrophobic PEDOT chains, which cause the phase separation between the chains. Consequently, as the dipoles of additive increased the coulomb interaction reduced increasingly, then because of loosely structure the PEDOT chains during film formation reoriented and leaving high conductivity of thin film on the surface of the substrate.

On the other hand, by increasing the molecular size of the co-solvent, the space between PEDOT and PSS chains increased. Then as the boiling point of co-solvent increased, the length of the time that co-solvent exist in between PEDOT and PSS chains raised (figure 4), thereby creating an opportunity for a favorable morphological rearrangement to a decreased resistance between dried particles, thus increasing the overall conductivity of the film. However, the boundaries between the dried particles in an ink-jet printed film contribute significantly to the overall resistivity of the film. Maximum conductivity is achieved by maximizing the contact between dried particles in PEDOT:PSS films. Therefore the conductivity enhancement

| Ink | Surface resistance ($\Omega \cdot \text{cm}^{-2}$)/1 layer | Surface resistance ($\Omega \cdot \text{cm}^{-2}$)/3 layers |
|-----|---------------------------------------------|---------------------------------------------|
| 1   | 48.5                                       | 47.1                                       |
| 2   | 48.1                                       | 47.4                                       |
| 3   | 47.5                                       | 46.5                                       |
| 4   | 47.2                                       | 45.7                                       |
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is strongly dependent on the chemical structure, dipoles, and boiling point of co-solvent. By increasing dipole moments, and boiling point of co-solvent, the thin film conductivity on the surface of the substrate increase.

3.5. Effect of thickness on electrical and optical properties

Table 4 shows that the dependency of the electrical properties of the material to the number of runs performed with the PEDOT:PSS ink-jet inks. By increasing the number of printing runs, the conductivity of the printed film increase. This raising in conductivity might be due to increase the thickness and uniformity of the pattern by build-up a greater concentration of the conductive PEDOT:PSS on the substrate.

As the three runs of PEDOT:PSS ink-jet printed films had the optimum conductive properties, therefore, the optical properties of that optimum printed film were assessed by UV–VIS absorption spectroscopy. Figure 5 illustrates that the average transmittance of PEDOT:PSS ink-jet printed films (Ink1 to Ink4) on the visible light region slightly decreased by increasing not only the molecular weight of co-solvents but also the particle size distribution of PEDOT:PSS, for example the transparency of the Ink1, which formulated with DEG is 87.58% and for Ink 4 that consist PEG is 86.62%.

It was assumed that, by increasing the particle size distribution of PEDOT:PSS the thickness of the printed film raised, hence the light reflection faintly increased. The ink-jet printed PEDOT:PSS films onto the flexible substrate exhibited high transparency within the visible wavelength region and ideal for use in optoelectronic devices. Therefore, it is inferred that adding co-solvents to the PEDOT:PSS based ink-jet inks had a minor effect on optical properties of the PEDOT:PSS ink-jet printed film.

3.6. Morphology (AFM, SEM and TEM)

AFM topography images were obtained for different ink-jet printed films (Ink1 to Ink4), that contain various co-solvent in their formulation, to allow studies possible changes in morphology on a nanometer scale. The morphologies of the four samples were compared as measured by AFM topography images (figure 6). Therefore, the AFM images and results of the Ink1 to Ink4 printed films (table 5) confirmed that the roughness of PEDOT:PSS ink-jet printed films increased from 2.9 to 3.55 nm at root mean square (RMS) by increasing the molecular weight of co-solvent and PEDOT:PSS particle size distribution. Furthermore, the AFM images show a grain like structure of PEDOT:PSS film. Grain like structure was matched to the previous studies, which can be explained by the self-assembly and consequently increased inter-chain interaction occurring in the film form by ink-jet printing process [4, 44]. Therefore, adding co-solvent in the ink formulation effect on the roughness and morphology of the printed PEDO:PSS films.

SEM images of the ink-jet printed PEDOT:PSS films (Ink1–Ink4) are depicted in figure 7 demonstrates the addition co-solvent effect on the morphology of the ink-jet printed PEDOT:PSS. In SEM image the size of cauliflower
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like structures increased by increasing the boiling point and molecular weight of used co-solvent in ink-formulation.

TEM image of the optimum PEDOT:PSS ink is depicted in figure 8 that demonstrates micelles of PEDOT:PSS particles in the ink and clearly demonstrates the well dispersed particles with a minimal size variation (200 nm) in the ink.

4. Conclusions

Studies on PEDOT:PSS ink-jet inks that blended with different organic co-solvents, which have different structure, dipole moment and boiling point, have shown that conductivity, transparency and roughness of ink-jet printed films can be increased by increasing the molecular weight, dipole moment and boiling point. The increasing in the electrical conductivity can be related to the screening effect of the (polar) solvent that improved the morphology of the film either by expanding the coiled PEDOT:PSS that increased conjugation length or made the polarones more delocalized and changes the charge transport properties. The best method of increasing electrical conductivity of PEDOT:PSS ink-jet printed films is mixing the PEDOT:PSS ink with polyethylene glycol. Therefore, adding co-solvent not only may played an important role in the physical properties of the PEDOT:PSS ink-jet inks but also in improving the conductivity and transparency of the printed films. On the other hand, by increasing the number of printing runs, the conductivity and thickness of the printed films increased. This raising might be due to uniformity of the pattern by build-up a greater concentration of the conductive PEDOT:PSS on the substrate.

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References

[1] Bubnova O, Khan Z U, Wang H, Braun S, Evans D R, Fabretto M, Hojati T P, Dagnelund D, Arlin J B and Geerts Y H 2014 Semi-metallic polymers Nat. Mater. 13 190
[2] Friend R H et al 1999 Electroluminescence in conjugated polymers Nature 397 121–8
[3] Heuer H W, Wehrmann R and Kirchmeyer S 2002 Electrochromic window based on conducting poly(3,4-ethylenedioxythiophene)–poly(styrene sulfonate) Adv. Funct. Mater. 12 89
[4] Chou W Y et al 2007 Polymer light-emitting diodes with thermal inkjet printed poly(3,4-ethylenedioxythiophene)–polystyrenesulfonate as transparent anode Thin Solid Films 515 3718
[5] Zhang Y, Cui W, Zhu Y, Zu F, Liao L, Lee S T and Sun B 2015 High efficiency hybrid PEDOT:PSS/nanostructured silicon Schottky junction solar cells by doping-free rear contact Energy Environ. Sci. 8 297
[6] Nilsson D, Kugler T, Svensson P O and Berggren M 2002 An all-organic sensor–transistor based on a novel electrochemical transducer concept printed electrochemical sensors on paper Sensors Actuators B 86 193
[7] Chen M, Nilsson D, Kugler T, Berggren M and Remonen T 2002 Electric current rectification by an all-organic electrochemical device Appl. Phys. Lett. 81 2011
[8] Ellmer K 2012 Past achievements and future challenges in the development of optically transparent electrodes Nat. Photon. 6 809
[9] Lim J A, Kim J H, Qiu L, Lee W H, Lee H S, Kwak D and Cho K 2010 Inkjet-printed single-droplet organic transistors based on semiconductor nanowires embedded in insulating polymers Adv. Funct. Mater. 20 3292
[10] Wu Z et al 2004 Transparent, conductive carbon nanotube films Science 305 1273

Figure 7. SEM images of printed different inkjet ink formulation of PEDOT:PSS.

Figure 8. TEM image of the optimal PEDOT:PSS ink-jet ink.
[11] Zhang M, Fang S, Zakidov A A, Lee S B, Aliev A E, Williams C D, Atkinson K R and Baughman R H 2005 Strong, transparent, multifunctional, carbon nanotube sheets Science 309 1215

[12] Yang S B, Kong B S, Jung D H, Baek Y K, Han C S, Oh S K and Jung H T 2011 Recent advances in hybrids of carbon nanotube network films and nanomaterials for their potential applications as transparent conducting films Nanoscale 3 1361

[13] Wu J, Becerril H A, Bao Z, Liu Z, Chen Y and Peumans P 2008 Organic solar cells with solution-processed graphene transparent electrodes Appl. Phys. Lett. 92 263302

[14] Arco G D L, Zhang Y, Schlenker C W, Ryu K, Thompson M E and Zhou C 2010 Continuous, highly flexible, and transparent graphene films by chemical vapor deposition for organic photovoltaics ACS Nano 4 2865

[15] Bae S et al 2010 Roll-to-roll production of 30-inch graphene films for transparent electrodes Nat. Nanotechnol. 5 574

[16] Kim K S, Zhao Y, Jang H, Lee S Y, Kim J M, Kim K S, Ahn J H, Kim P, Choi J Y and Hong B H 2009 Large-scale pattern growth of graphene films for stretchable transparent electrodes Nature 457 706

[17] Kang M G, Kim M S, Kim J and Guo L J 2008 Organic solar cells using nanoimprinted transparent metal electrodes Adv. Mater. 20 4408

[18] Lee J Y, Connor S T, Cui Y and Peumans P 2008 Solution-processed metal nanowire mesh transparent electrodes Nano Lett. 8 689

[19] Zhu R et al 2011 Fused silver nanowires with metal oxide nanoparticles and organic polymers for highly transparent conductors ACS Nano 5 9877

[20] Hu L, Wu H and Cui Y 2011 Metal nanogrids, nanowires, and nanofibers for transparent electrodes MRS Bull. 36 760

[21] Zou J, Li C Z, Chang C Y, Yip H L and Jen A K Y 2014 Interfacial engineering of ultrathin film transparent electrode for flexible organic photovoltaic cells Adv. Mater. 26 3618

[22] Cao Y, Yu G, Zhang C, Menon R and Heeger A J 1997 Polymer light-emitting diodes with polyelethylene dioxythiophene–polystyrene sulfonate as the transparent anode Synth. Met. 87 171

[23] Ouyang J, Chu C W, Chen F C, Xu Q and Yang Y 2005 High-conductivity poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) film and its application in polymer optoelectronic devices Adv. Funct. Mater. 15 203

[24] Simpson J, Kirchmeyer S and Reuter K 2005 AIME/AC Fall Technical Conf. and 19th Int. Vacuum Web Coating Conf. 2005

[25] Kirchmeyer S and Reuter K 2005 Scientific importance, properties and applications of poly(3,4-ethylenedioxythiophene) J. Mater. Chem. 15 2077

[26] Lang U, Müller E, Naujoks N and Dual J 2009 Microscopical investigations of PEDOT:PSS thin films Adv. Funct. Mater. 19 1215

[27] Crispin X, Marciniak S, Osikowicz W, Zotti G, Gon A W D, Louwet F, Fahlman M, Groenendaal L, Schryver F D and Salaneck W R 2003 Conductivity, morphology, interfacial chemistry, and stability of poly[3,4-ethylenedioxythiophene]–poly(styrene sulfonate): a photoelectron spectroscopy study J. Polym. Sci. B 41 2561

[28] Kim N, Kee S, Lee S H, Lee B H, Kahng Y H, Jo Y R, Kim B J and Lee K 2014 Highly conductive PEDOT:PSS nanofilms induced by solution-processed crystallization Adv. Mater. 26 2268

[29] Xia Y and Ouyang J 2010 Significant conductivity enhancement of conductive poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) films through a treatment with organic carboxylic acids and inorganic acids ACS Appl. Mater. Interfaces 2 474

[30] Stöcker T, Köhler A and Moos R 2012 Why does the electrical conductivity in PEDOT:PSS decrease with PSS content? A study combining thermoelectric measurements with impedance spectroscopy J. Polym. Sci. B 50 976

[31] Alemu D, Wei H-Y, Ho K-C and Chu C-W 2012 Energy Environ. Sci. 5962

[32] Döbbelin M, Marcilla R, Salsamendi M, Pozo-Gonzalo C, Carrasco P M, Pomposo J A and Mecerreyes D 2007 Influence of ionic liquids on the electrical conductivity and morphology of PEDOT:PSS films Chem. Mater. 19 2147

[33] Fan B, Mei X and Ouyang J 2008 Significant conductivity enhancement of conductive poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) films by adding anionic surfactants into polymer solution Macromolecules 41 5971

[34] Jönsson S K M, Birgerson J, Crispin X, Greczynski G, Osikowicz W, Gon A W D, Salanec W R and Fahlman M 2003 The effects of solvents on the morphology and sheet resistance in poly(3,4-ethylenedioxythiophene)–polystyrene sulfonic acid (PEDOT–PSS) films Synth. Met. 139 131

[35] Crispin X, Jakobsson F L E, Crispin A, Grim P C M, Andersson P, Volodin A, Hasendonck C, Auweraer M V, Salanec W R and Berggren M 2006 The origin of the high conductivity of poly(3,4-ethylenedioxythiophene)–poly(styrene sulfonate) (PEDOT–PSS) plastic electrodes Chem. Mater. 18 4354

[36] Yan H, Jo T and Okuzaki H 2009 Highly conductive and transparent poly(3,4-ethylenedioxythiophene):poly(4-styrene sulfonate) (PEDOT:PSS) thin films Polym. J. 41 1028

[37] Xia Y, Zhang H and Ouyang J 2010 Highly conductive PEDOT:PSS films prepared through a treatment with zwitterionics and their application in polymer photovoltaic cells J. Mater. Chem. 20 9740

[38] Pingree L S C, MacLeod B A and Ginger D S 2008 The changing face of PEDOT:PSS films: substrate, bias, and processing effects on vertical charge transport J. Phys. Chem. C 112 7922

[39] Timpanaro S, Kemerink M, Touwslager F J, De Kok M M and Schrader S 2004 Morphology and conductivity of PEDOT/ PSS films studied by scanning–tunnelling microscopy Chem. Phys. Lett. 394 339

[40] Wang G F, Tao X M, Xin J H and Fei B 2009 Modification of conductive polymer for polymeric anodes of flexible organic light-emitting diodes Nano Res. Lett. 4 613

[41] Ma K X, Ho C H, Zhu F R and Chung T S 2000 Investigation of surface energy for organic light emitting polymers and indium tin oxide Thin Solid Films 371 140

[42] Soleimani-Gorgani A 2016 Printing on Polymers: Fundamentals and Applications (New York: Elsevier) p 231

[43] Calvert P 2001 Inkjet printing for materials and devices Chem. Mater. 13 3299

[44] Greczynski G, Kugler T and Salanec W R 1999 Characterization of the PEDOT–PSS system by means of x-ray and ultraviolet photoelectron spectroscopy Thin Solid Films 354 129