Spray-coated contacts from an organic charge transfer complex solution for organic field-effect transistors

S. Georgakopoulos,^a A. Pérez-Rodríguez,^a A. Campos,^a I. Temiño,^a S. Galindo,^a E. Barrena,^a C. Ocal^a and M. Mas-Torrent^{a,b*}

Abstract

We demonstrate the deposition of films of the conducting charge transfer complex TTF-TCNQ from solution by spray coating. The benefit of spray coating is the ability to process large volumes of solution, therefore allowing the utilisation of compounds with very low solubility. The sheet resistance in the TTF-TCNQ film is similar to that of the commonly used organic PEDOT:PSS electrodes, with the added benefit of room temperature deposition and no additional thermal treatments. Spray coated TTF-TCNQ is used as source and drain electrodes for transistors based on the organic semiconductor C8-BTBT, achieving similar performances in terms of mobility and turn-on voltage than when conventional contacts of MoO_x/Au are used, whilst exhibiting a slight improvement in the linearity of the output characteristics.

^a Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus de la UAB, 08193, Bellaterra, Spain.

^b CIBER-BBN, Campus UAB, 08193 Bellaterra, Spain.

* E-mail: mmas@icmab.es

1. Introduction

The practical production of electronic devices by printing requires the utilisation of conductors deposited from solution, over large areas and ideally at not excessively high temperatures. Various oxide (such as Zn or In based) formulations can be deposited from solution and exhibit high performance, but require high temperature processing in the range of 100-500 °C, which can limit applications onto flexible substrates and could damage the organic semiconductor layer.¹ Silver nanoparticle inks can be printed and thermally annealed at 120 °C.² Electrodes from aqueous solutions of the doped conducting polymer poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate (PEDOT:PSS) have been prepared achieving a typical sheet resistance of 2 k Ω -cm although they are also thermally treated above 100 °C to evaporate the solvent and improve performance.³⁻⁴ Conducting charge transfer (CT) complexes consisting of an organic acceptor and an organic donor molecule provide a clear alternative.⁵ A notable example is tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) (Fig. 1b), which has been proven to perform well as an electrical contact to organic semiconductors resulting in low contact resistances and efficient charge injection.⁶ Additionally, the work function of CT complexes can be finely adjusted by the appropriate selection of their constituents to match the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) level of the desired semiconductor and eliminate hence injection barriers at the interface.⁷ However due to the limited solubility of CT complexes, thermal evaporation is usually utilised to deposit them.⁸⁻¹⁰ To date, the solution processing of TTF-TCNQ has only been achieved either by the sequential deposition of the individual donor and acceptor solutions¹¹ or by the formation of nanoparticle dispersions.¹²

Here we demonstrate that conductive films of TTF-TCNQ can be deposited from a solution of the CT complex by spray-coating. The advantage of spray-coating is the ability to process large solution volumes in a short time and to deposit over a large area.¹³ Consequently, spray coating is an ideal technique for the deposition of compounds with low solubility, which cannot be processed by traditional

techniques such as ink-jet printing or solution shearing, where a low volume of a concentrated solution of the compound is required. Additionally, the deposition is performed at room temperature with no need of further thermal treatments as the solvent used is highly volatile. As a proof of concept, organic field-effect transistors (OFETs) based on C8-BTBT:polystyrene^{14,15} (C8-BTBT stands for 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene) as active layer and spray-coated TTF-TCNQ top-contact source/drain electrodes were fabricated. The devices exhibited high performances comparable to those achieved with conventional evaporated MoO_x/Au contacts.

2. Experiment details

2.1 Spray coating of TTF-TCNQ

TTF-TCNQ (Sigma Aldrich) was dissolved in HPLC grade acetone (0.30 mg/ml) by strong agitation in an ultrasonic bath (for four hours). The TTF-TCNQ solution remains stable over time. No precipitation or colour changes were observed during one month of solution storage. The spray-coating setup is shown in Fig. 1a. It consists of a masked substrate, in this case sandwiched between a magnetic base and a metal mask, and an airbrush that utilises pressurised nitrogen to aerosolise the TTF-TCNQ solution. The area of the metal mask used was (70 x 70) mm². The area of the targeted substrate was (18 x 20) mm². Additional surrounding pieces of identical thickness were placed to maintain mask planarity. The mask has to be kept planar without gaps underneath since they cause vibrations and bad contact because of the air flow. An airbrush (Sagola junior 140, 0.8 mm nozzle diameter) was fixed 18-19 cm above the sample (nozzle to sample surface separation) and 40 ml of TTF-TCNQ solution were deposited. The deposited layer thickness is very sensitive to the nozzle to sample separation: separation distances over 20 cm result in a significantly reduced film thickness, and distances less than 17 cm cause the formation of liquid droplets on the sample surface. The optimum distance can be tuned by adjusting the pressure of the nitrogen gas to which it is proportional. The process was performed at room temperature, in

ambient conditions, and took approximately 4 minutes (10 ml/min solution flow rate) at a nitrogen pressure of 1.5 bar. The spray-coating was also performed at an elevated temperature of 80 °C, without giving rise to notable differences in the TTF-TCNQ sheet resistance.

The main area limiting factor is the spray jet coverage and not the mask dimensions. To characterize the coating coverage, TTF-TCNQ was spray coated onto Si/SiO₂ substrates with patterned four point probe Cr/Au bottom contacts (5 and 40 nm thick, respectively) patterned by photolithography and lift-off (no mask was used for the spraying).

TTF-TCNQ is also soluble in THF in a concentration of up to 0.9 mg/ml. THF is a more aggressive solvent and would cause damage to the underlying semiconductor layer used in this work, however it might be applicable to processes with other materials. Also, the sheet resistance values measured in TTF-TCNQ films deposited from a THF solution were four times higher than those deposited from acetone.

2.2 Organic Field-Effect Transistor Fabrication

OFETs were fabricated in the Bottom-Gate Top-Contact configuration. Si_{n++}/SiO₂ substrates (Si-Mat, 200 nm oxide thickness) were cleaned by immersion into acetone and isopropanol in an ultrasonic bath for 5 minutes each. For the active layer solution, C8-BTBT (Sigma-Aldrich, used as received) was blended with polystyrene (Sigma Aldrich, Molecular weight 10000 g/mol) in a ratio of 4:1 and dissolved in anhydrous chlorobenzene (2 % wt). The solution was coated by Bar-Assisted Meniscus Shearing as previously reported at 105 °C and at 10 mm/s.¹⁴ The sample was placed on a magnetic base, covered with a metallic mask (stainless steel, 50 µm thickness) and, subsequently, exposed to TTF-TCNQ spray-coating. The transistor channels formed were 4 mm wide with lengths of 60, 80 and 100 µm. For comparison, devices with MoO_x/Au (15 nm/100 nm) top-contact electrodes were also fabricated.

2.3 Scanning Probe Microscopy Characterization:

Scanning probe microscopy (SPM) measurements were carried out at room temperature using different instruments with the instrument Dulcinea from Nanotec Electrónica. All data was analysed by using the WSxM software. Both Amplitude modulation atomic force microscopy (AM-AFM, dynamic mode with fixed frequency) and contact AFM working in ambient conditions were used to investigate the surface morphology.

Electrostatic probe force (EFM) is a dynamic mode that measures the electrostatic force between a metallic tip and the sample. The tip and sample are not in direct contact but are electrically connected via electronics. As a result, their Fermi levels align, creating an SP, and thus, a tip-sample electrostatic force develops. EFM was used to accurately determine local variations in surface contact potential difference (ΔCPD). The electrostatic force (F_{el}) between a conductive AFM tip and a close metallic surface is given by $F_{el} = -\partial C/\partial z (V_{DC} - V_{CPD})^2$. As the phase shift of an oscillating probe is proportional to the force gradient, it will also present a quadratic dependence with V_{DC} with the parabola centered in V_{CPD} . In this work alternate Phase- V_{DC} were acquired in the TTF:TCNQ electrode and in a highly oriented pyrolytic graphite (HOPG) reference sample, in order to assure reproducibility and to obtain an accurate value of the TTF:TCNQ electrode workfunction. Conducting CrPt diamond coated Si tips (by Budgetsensors) mounted on cantilevers with $k = 3\text{N/m}$ were employed.

The CPD values are extracted from the position of the maximum in the parabolic dependence of the electrostatic force with the applied voltage measured at a minimum of 15 locations and several curves taken at each position.

3- Results and Discussion

A solution of TTF-TCNQ in acetone ($c = 0.3$ mg/ml) was sprayed as detailed in the experimental section. The surface of the TTF-TCNQ sprayed layer consists of plate and needle shaped crystals of approximate length of one micrometre (Fig. 1c, and Fig. S3a). X-ray analysis shows two peaks corresponding to d-spacing of $9.1 \text{ \AA}$ (Fig. S1), coinciding with reports of evaporated TTF-TCNQ films and indicating that the conducting *ab* plane of the crystals lies in parallel with the substrate.⁹

Figure 1. (a) Spray-coating set-up. (b) Molecular structure the C8-BTBT semiconductor and TTF-TCNQ charge transfer salt. (c) SEM image of TTF-TCNQ layer surface.

The sheet resistance was measured as a function of the radial distance from the centre of focus of the spray jet (Fig. 2a) and was found to increase from $3 \text{ k}\Omega\cdot\text{cm}$ at a distance of 0.6 cm to $6 \text{ k}\Omega\cdot\text{cm}$ at a distance of 1.5 cm (Fig. 2b). These values are very similar to reports on evaporated TTF-TCNQ films, where sheet resistances of $4 \text{ k}\Omega\cdot\text{cm}$ (300 nm thick films) were found.¹⁰ Thus, for this particular experimental setup, the effective coating area is approximately 3 cm in diameter.

Figure 2. (a) Si/SiO₂ substrates with covered four-point probe structures made out of Cr/Au. The spray jet was focused at the centre and the sheet resistance was measured along the coloured lines, as a function of distance from the centre. The values are plotted in (b). Filled squares represent the initial measurements and empty squares measurements of the same samples one year later.

As a proof-of-concept, the spray-coated TTF-TCNQ electrodes were used as contacts in OFETs. C8-BTBT was chosen as organic semiconductor since this material exhibits high field-effect mobilities exceeding 1 cm²/V·s.^{16,17} However, C8-BTBT tends to suffer contact issues due to its high Ionisation Potential (IP) of 5.5 eV.¹⁸ To our knowledge, the most efficient top contact is achieved by utilising a MoO_x interfacial layer between C8-BTBT and Au,^{19,20} which raises the electrode work function to 5.6 eV.²¹ An alternative type of contact has been achieved by doping the contact interface with FeCl₃, which results in the generation of mid band-gap states and tunneling through the high Schottky barrier.²² Solution-processed graphene oxide bottom-contacts have been also utilised though exhibiting non-linear output characteristics.²³

OFETs were fabricated on Si_{n++}/SiO₂ substrates with a bottom-gate top-contact configuration (Figure 3a). Blends of C8-BTBT with polystyrene in a ratio of 4:1 and dissolved in anhydrous chlorobenzene (2 % wt) were casted by bar-assisted meniscus shearing as previously reported.¹⁴ C8-BTBT forms large plate-like domains with sizes of hundreds of microns (Fig. S2). Afterwards, TTF-TCNQ

was sprayed on the top through a mask to fabricate the source and drain contacts (Fig.3b). For comparison, devices with top MoO_x/Au contacts were also fabricated.

Figure 3. (a) Cross-section of the device configuration of the transistor. (b) Microscope image of transistor channel with visible C8-BTBT layer and TTF-TCNQ electrodes.

In order to examine the possible impact of the spray deposition on the morphology of the semiconductor layer and the quality of the contact, both the electrode edge and the channel were analysed by Atomic Force Microscopy (AFM). Typical topographic images are presented in Fig. 4 for the two regions. The profile relief in Fig. 4a passing along both areas reveals that the crystallites forming the TTF-TCNQ coating have heights ranging between 30 and 200 nm. Fig. 4b shows the edge of the OFET channel containing a large part of the active region and a portion of the electrode. The extreme flatness of the semiconductor layer in the channel (Fig. 4c) and at the electrode edge (Fig. 4d) is a clear hint supporting that its morphology is not affected by the electrode deposition.

Figure 4: (a) Topographic image of the electrode and most of the channel area ($L = 50\mu\text{m}$). (b) Line profile taken along the black segment in the image. Morphologic details of the central part of the channel (c) and of a region including the TTF-TCNQ electrode edge (d).

OFETs contacted with MoO_x/Au exhibit saturation mobilities in the range of $0.1\text{--}2\text{ cm}^2/\text{V}\cdot\text{s}$ with a mean value of $0.7\text{ cm}^2/\text{V}\cdot\text{s}$ over 12 measured OFETs on 4 substrates (Fig. S4a). The turn-on voltage was almost 0 V, subthreshold swing of 2 V/decade, and on/off ratio of 10^6 (Fig. 5a). The OFET parameters are summarized in table 1. Output characteristics show low-linearity at low drain voltage (Fig. 5b inset). OFETs fabricated with TTF-TCNQ top-contacts exhibit peak saturation mobilities in the range of $0.2\text{--}1.4\text{ cm}^2/\text{V}\cdot\text{s}$ with a mean value on $0.7\text{ cm}^2/\text{V}\cdot\text{s}$ over 17 measured OFETs on 6 substrates. The turn-on voltage, subthreshold swing and on/off ratio are similar to the MoO_x/Au OFETs. Nonetheless, the output characteristic exhibits noticeably better linearity at low drain voltages than with MoO_x contacts. OFETs with both types of contact were stable over a month in ambient conditions (Fig. S4d).

Figure 5. (a) Forward and reverse transfer characteristics of OFETs based on C8-BTBT and MoO_x/Au evaporated contacts (black lines) or TTF-TCNQ spray coated contacts (red lines). The gate currents are represented with dashed lines. The OFET channels are 4 mm wide and 100 μm long. The drain voltage is -30V. Representative characteristics were chosen for OFETs of similar saturation mobilities (0.6 cm²/V·s). (b) Output characteristics of the same devices for gate voltages of 0 to -40 V in steps of -10V. The inset shows magnification of the characteristics for V_{GS} = -40V.

Electrodes	μ_{SAT} range (mean)	V _{ON} range (mean)	R _c range (mean)	I _{DS-ON/OFF}
MoO _x /Au	0.1 to 2 (0.7) cm ² /V·s	-0.22 to -3.10 (-1.3) V	18 to 20 (19) kΩ·cm	10 ⁶
TTF-TCNQ	0.2 to 1.4 (0.7) cm ² /V·s	0.18 to -3.29 (-0.9) V	37 to 67 (53) kΩ·cm	10 ⁶

Table 1. Summary of OFET parameters. The mobility and turn-on voltage ranges and mean values and were extracted from 12 OFETs on 4 different substrates for MoO_x/Au and 17 OFETs on 6 different substrates for TTF-TCNQ. The contact resistances were calculated for 3 OFET of similar mobilities for each case.

The contact resistance was estimated by the Y-function method²⁴ which permits the extraction of contact resistance from a single device, though the dependence on gate voltage cannot be ascertained. The contact resistance for the MoO_x/Au OFETs was estimated to be 53±16 kΩ·cm, which is

slightly higher than reported values, which are in the range of 8-50 k Ω ·cm (gate voltage dependent, extracted by gated transmission line method) for similar OFETs of C8-BTBT with MoO_x/Au contacts.¹⁹ For the devices with TTF-TCNQ electrodes the extracted contact resistance in this work was 18 $\pm$ 3 k Ω ·cm, almost three times lower than with MoO_x/Au.

Commonly, the reported work function (ϕ) values of organic CT complexes are inferred from considering the energy of the HOMO and LUMO of the isolated components and might differ from that of the compound. To have a realistic value, the work function of the TTF-TCNQ employed here was experimentally evaluated from the measured contact potential difference (CPD) between the electrodes of the particular devices and a conductive AFM tip. The CPD values are extracted from the position of the maximum in the parabolic dependence of the electrostatic force with the applied voltage (see Experimental Details) measured at a minimum of 15 locations and several curves taken at each position.²⁵ In order to discard tip work function uncertainty and any possible tip change, the absolute value of the ϕ was determined, under the same conditions and with the same tip, using as a reference a highly oriented pyrolytic graphite (HOPG) sample²⁶ before and after measuring over the TTF-TCNQ electrode (Fig. 6). Though the obtained $\phi \approx 4.9 \pm 0.1$ eV is somehow higher than the reported range (4.64 to 4.78 eV),⁹ this value is insufficiently high to account for the more efficient contact with the semiconductor and lower contact resistance as compared to devices with MoO_x/Au electrodes. If there was vacuum level alignment between C8-BTBT and TTF-TCNQ, there would be a significant injection barrier of 0.8 eV which would noticeably affect device performance. According to our results this is not the case, as TTF-TCNQ actually seems to form a better contact than MoO_x/Au. Therefore, it must be concluded that the specific electronic coupling of both organic compounds at the, semiconductor/TTF-TCNQ interface, favours the hole injection most likely due to the formation of interface dipoles. Such dipoles have been observed for a variety of organic-organic and organic-metal interfaces and can exceed 1 eV.²⁷ For organic-organic interfaces, it has been shown that charge-transfer as well as polarization

effects are factors contributing to the sign and magnitude of the dipole.²⁸ Interface dipoles are indeed commonly observed in donor-acceptor systems such as in multilayers of TTF/TCNQ, where the HOMO of the TTF donor and the LUMO of the TCNQ acceptor align at the interface between the two materials.²⁹ It is likely that in our case at the interface between the TTF-TCNQ and C8-BTBT films a dipole is induced. Another cause that could lead to a more efficient contact could be the intermixing of the organic metal with the organic semiconductor. This effect was previously observed in solution grown single crystals of a TTF derivative semiconductor on evaporated TTF-TCNQ contact, which gave rise to devices exhibiting a lower contact resistance.⁸

Figure 6: Phase $-V_{\text{Bias}}$ curves performed on top of the TTF-TCNQ electrode and on a reference HOPG sample. The corresponding work function values, obtained from the parabolic fit of the data, are given at the top panel along with that of gold ($\phi \approx 5.1$ eV), where the width of the colour scales indicate the statistical error of the measurements.

4. Conclusions

In summary we demonstrate the deposition of TTF-TCNQ charge transfer complex from solution by spray-coating. The resulting films exhibit the same crystal phase and sheet resistance as the evaporated TTF-TCNQ ones. Such values are also similar to the commonly used PEDOT:PSS electrodes with the added benefit here that there is no need of applying additional thermal treatments. OFETs were fabricated with C8-BTBT top contacted with spray-coated TTF-TCNQ, as well as with conventional evaporated MoO_x/Au source/drain contacts. Performance was similar between the two types of contacts in terms of mobility (mean of 0.7 cm²/V·s), turn-on voltage (near 0 V), subthreshold swing (2 V/decade), and on/off ratio (10⁶). The only notable difference was better linearity in output characteristics and lower estimated contact resistance for the TTF-TCNQ contacts, which has been attributed to the formation of interface dipoles at the organic semiconductor/organic metal interface.

Acknowledgements

This work was mainly funded by the ERC StG 2012-306826 e-GAMES project. The authors also thank the Networking Research Center on Bioengineering, Biomaterials and Nanomedicine (CIBER-BBN), the DGICT (Spain) with projects BE-WELL CTQ2013-40480-R, FANCY CTQ2016-80030-R and MAT2016-77852-C2-1-R, Generalitat de Catalunya 2014-SGR-17, and the Spanish Ministry of Economy and Competitiveness, through the “Severo Ochoa” Programme for Centres of Excellence in R&D (SEV-2015-0496). A.C., I.T. and A. P.-R. are enrolled in the Materials Science PhD program of Universitat Autònoma de Barcelona and acknowledge FPU fellowship from the Ministry.

References

- 1 R. M. Pasquarelli, D. S. Ginley and R. O’Hayre, *Chem. Soc. Rev.*, 2011, **40**, 5406–5441.
- 2 G. Chinga-Carrasco, D. Tobjörk and R. Österbacka, *J. Nanoparticle Res.*, 2012, **14**, 1213.
- 3 M. C. Choi, Y. Kim and C. S. Ha, *Prog. Polym. Sci.*, 2008, **33**, 581–630.

- 4 Z. Xiong and C. Liu, *Org. Electron.*, 2012, **13**, 1532–1540.
- 5 K. P. Goetz, D. Vermeulen, M. E. Payne, C. Kloc, L. E. McNeil and O. D. Jurchescu, *J. Mater. Chem. C*, 2014, **2**, 3065–3076.
- 6 R. Pfattner, C. Rovira and M. Mas-Torrent, *Phys. Chem. Chem. Phys.*, 2015, **17**, 26545–26552.
- 7 Y. Takahashi, T. Hasegawa, Y. Abe, Y. Tokura and G. Saito, *Appl. Phys. Lett.*, 2006, **88**, 73504.
- 8 R. Pfattner, M. Mas-Torrent, C. Moreno, J. Puigdollers, R. Alcubilla, I. Bilotti, E. Venuti, A. Brillante, V. Laukhin, J. Veciana and C. Rovira, *J. Mater. Chem.*, 2012, **22**, 16011–16016.
- 9 K. Shibata, H. Wada, K. Ishikawa, H. Takezoe and T. Mori, *Appl. Phys. Lett.*, 2007, **90**, 193509.
- 10 K. Shibata, K. Ishikawa, H. Takezoe, H. Wada and T. Mori, *Appl. Phys. Lett.*, 2008, **92**, 23305.
- 11 B. Mukherjee and M. Mukherjee, *Langmuir*, 2011, **27**, 11246–11250.
- 12 D. de Caro, K. Jacob, H. Hahoui, C. Faulmann, L. Valade, T. Kadoya, T. Mori, J. Fraxedas and L. Viau, *New J. Chem.*, 2011, **35**, 1315–1319.
- 13 D. Vak, S. Kim, J. Jo, S. Oh, S. Na, J. Kim and D.-Y. Kim, *Appl. Phys. Lett.*, 2007, **91**, 81102.; G.-P. Rigas, M. M. Payne, J. E. Anthony, P. N. Horton, F. A. Castro, M. Shkunov, *Nat. Commun.* **2016**, **7**, 13531.
- 14 I. Temiño, F. G. Del Pozo, M. R. Ajayakumar, S. Galindo, J. Puigdollers and M. Mas-Torrent, *Adv. Mater. Technol.*, 2016, **1**, 1600090.
- 15 F. G. del Pozo, S. Fabiano, R. Pfattner, S. Georgakopoulos, S. Galindo, X. Liu, S. Braun, M. Fahlman, J. Veciana, C. Rovira, X. Crispin, M. Berggren and M. Mas-Torrent, *Adv. Funct. Mater.*, 2016, **26**, 2379–2386.
- 16 T. Uemura, Y. Hirose, M. Uno, K. Takimiya and J. Takeya, *Appl. Phys. Express*, 2009, **2**, 111501.
- 17 Y. Yuan, G. Giri, A. L. Ayzner, A. P. Zoombelt, S. C. B. Mannsfeld, J. Chen, D. Nordlund, M. F. Toney, J. Huang and Z. Bao, *Nat. Commun.*, 2014, **5**, 3005.
- 18 H. Ebata, T. Izawa, E. Miyazaki, K. Takimiya, M. Ikeda, H. Kuwabara and T. Yui, *J. Am. Chem. Soc.*, 2007, **129**, 15732–15733.
- 19 M. Kano, T. Minari and K. Tsukagoshi, *Appl. Phys. Lett.*, 2009, **94**, 143304.
- 20 C. Liu, T. Minari, X. Lu, A. Kumatani, K. Takimiya and K. Tsukagoshi, *Adv. Mater.*, 2011, **23**, 523–526.
- 21 D. Kumaki, T. Umeda and S. Tokito, *Appl. Phys. Lett.*, 2008, **92**, 13301.
- 22 T. Minari, P. Darmawan, C. Liu, Y. Li, Y. Xu and K. Tsukagoshi, *Appl. Phys. Lett.*, 2012, **100**, 93303.
- 23 K. Kotsuki, H. Tanaka, S. Obata, S. Stauss, K. Terashima and K. Saiki, *Appl. Phys. Lett.*, 2014, **104**, 233306.
- 24 Y. Xu, T. Minari, K. Tsukagoshi, J. A. Chroboczek and G. Ghibaudo, *J. Appl. Phys.*, 2010, **107**, 114507.
- 25 C. Ocal, R. Bachelet, L. Garzón, M. Stengel, F. Sánchez and J. Fontcuberta, *Chem. Mater.*, 2012, **24**, 4177–4184.
- 26 W. N. Hansen and G. J. Hansen, *Surf. Sci.*, 2001, **481**, 172–184.
- 27 I. G. Hill, D. Milliron, J. Schwartz and A. Kahn, *Appl. Surf. Sci.*, 2000, **166**, 354–362.
- 28 I. Avilov, V. Geskin and J. Cornil, *Adv. Funct. Mater.*, 2009, **19**, 624–633.
- 29 R. J. Murdey, W. R. Salaneck, *Jap. J. Appl. Phys.* 2005, **44**, 3751.