DOI: 10.1002/ ((please add manuscript number))

Article type: Full Paper

Tuning Contact Resistance in Top-contact *p*- and *n*-type Organic Field Effect Transistors by Self-generated Interlayers

Tanmoy Sarkar, Basel Shamieh, Roy Verbeek, Auke Jisk Kronemeijer, Gerwin Gelinck and Gitti L Frey*

Tanmoy Sarkar, Basel Shamieh, Prof. Gitti L Frey

Department of Materials Science and Engineering, Technion – Israel Institute of Technology, Haifa 32000, Israel

E-mail: gitti@technion.ac.il

Roy Verbeek, Dr. Auke Jisk Kronemeijer, Prof. Gerwin Gelinck

Holst Centre, 5656 AE Eindhoven, The Netherlands

Department of Applied Physics, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

Keywords: organic electronics, self-generated interlayers, organic field-effect transistors, TLM

Abstract

Contact resistance significantly limits the performance of organic field-effect transistors (OFETs). Positioning interlayers at the metal/organic interface can tune the effective work-function and reduce contact resistance. Myriad techniques offer interlayer processing onto the metal pads in bottom-contact OFETs. However, most methods are not suitable for deposition on organic films and furthermore incompatible with deposition onto the organic semiconductor in top-contact architecture. Here we introduce a new, simple and versatile methodology for interlayer processing suitable also for top-contact OFETs. The method, demonstrated for both *p*- and *n*-type devices, leads to significant change in contact resistance. In this approach,

judiciously selected interlayer molecules are co-deposited as additives in the semiconducting polymer active layer. During the following top contact deposition, the additive molecules migrate from within the bulk film to the organic/metal interface due to additive-metal interactions. Additive migration continues until a thin continuous interlayer is completed. Formation of the interlayer is confirmed by x-ray photoelectron spectroscopy (XPS) and cross-section scanning transmission electron microscopy (STEM), and its effect on contact resistance by device measurements and transfer line method (TLM) analysis. We show that self-generated interlayers that reduce contact resistance in p-type devices, increase that of n-type devices, and vice versa, confirming the role of additives as interlayer materials that modulate the effective work-function of the organic/metal interface.

1. Introduction

Solution processed organic field-effect transistors (OFETs) are promising building blocks for future flexible electronic applications due to their cost-effective large-scale production combined with inherent mechanical flexibility.^[1] Accordingly, extensive research efforts are invested the development of protocols suitable for flexible device fabrication, roll-to-roll processing and printing,^[2] and the design and synthesis of high performance materials, specifically high mobility semiconductors,^[3] gate insulators^[4] and printable conductors.^[5] Importantly, because charge injection, extraction, and accumulation occur at the interfaces of different materials, new solution processing methodologies that control the structure and composition of interfaces in OFETs are also essential for high performances.^[6] One seminal interfacial electronic process that limits OFET performances is inefficient charge carrier injection from the source electrode to the organic semiconducting channel. Efficient injection into the organic semiconductor requires Ohmic contacts, i.e. barrier-less energy level alignment at the organic/metal interface.^[6a, 7] The Schottky barriers, and associated contact resistance, can

be reduced by aligning either the Highest Occupied Molecular Orbital (HOMO) of a p-type organic semiconductor, or the Lowest Unoccupied Molecular Orbital (LUMO) of an n-type organic semiconductor, with the work function of the metal electrode. Therefore, tuning the work function of the metal electrode is a practical approach for optimizing charge injection/extraction and hence device performance.^[8] A well-established strategy to tune the effective work function (EWF) at the organic/metal interface is by introducing ultrathin organic or inorganic interlayers between the metal contact and the organic semiconductor.^[9] In case of organic interlayer, polar molecules are placed at the semiconductor/metal interface and modify the EWF by imposing a dipole at the interface. The energy level alignment can be controllably tuned through the chemical composition of the molecule and the direction and magnitude of the dipole.^[7, 10] The most common technique of depositing organic interlayers onto substrates are thermal deposition^[11] and spin coating from orthogonal solvents.^[12] Another well-known technique is to deposit self-assembled monolayers (SAM) by immersing the substrate with metal electrodes in the SAM solution prior to the semiconductor layer deposition.^[6b, 13] All these methods involve additional processing steps, some of which are ~~difficult to scale up~~ cost-effective.

Recently, a self-generated methodology for interlayer formation was demonstrated for organic solar cells (OSC) and organic light emitting diodes.^{[13] [14]} In this technique, the interlayer molecules are blended as additives in the semiconducting polymer film. During the following metal electrode deposition at room temperature, these molecules migrate from within the film towards the organic/metal interface due to additive-metal interactions and self-generate the desired interlayer.^[15] The diffusivity of the additive through the active layer to the top interface depends on the chemical structure and size of the additive, the host matrix properties such as crystallinity density and chemical interactions with the additive, and temperature.^[16] Additive-substrate interactions can also affect the chemical potential field within the layer, and hinder

additive migration to the top contact.^[17] Using this methodology, self-generated interlayers of poly(ethylene glycol) (PEG) were shown to significantly improve the performances of OSCs and OLEDs.^[14d, 14e] In the case of OFETs, 2,3,4,5,6-pentafluorothiophenol (PFBT) was shown to migrate to the silver electrode of bottom contact top gate OFET and improve its performance significantly.^[18] The PFBT additive migrated towards the bottom organic/silver interface, while, upward migration of additives to modify the technically inaccessible organic/metal interface in top-contact OFETs, has not yet been reported.

Here, we demonstrate the use of self-generated interlayers for tuning the EWF and reducing the contact resistance of bottom-gate top-contact OFETs. To study the self-generated interlayer formation we fabricated p- and n-type bottom-gate top-contact OFETs based on diketopyrrolopyrrolethieno[3,2-b]thiophene copolymer (DPPT-TT) and Poly[[N,N'-bis(2-octyldodecyl)naphthalene-1,4,5,8-bis (dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)] (PNDI(2OD)2T) polymer, respectively. To modify the EWF of the buried organic/Ag (or Au) interface, we chose two thiol-capped additives: hexa(ethyleneglycol)-dithiol (HEG-DT) and 4-fluorobenzyl mercaptan (4-FM). Scanning transmission electron microscopy (STEM) and X-ray photoelectron spectroscopy (XPS) confirm the additives enrichment at the polymer/Ag interfaces after Ag deposition. Device measurements and transfer line method (TLM) analysis are used to evaluate the evolution of the contact resistance with interlayer formation. We find that self-generation of the additive interlayers at the polymer/metal interfaces significantly modifies the EWF, and that the EWF can be tuned to reduce the contact resistance leading to improved device performances.

2. Results and discussion

Work function is by definition a surface property and the EWF at interfaces depends on the compositions of the electrochemical and electrical properties of the interfacing materials, and the chemical and physical interactions between them.^[19] Hence, work function values measured

for bare metal surfaces or even distinctly prepared additive/metal interfaces do not necessarily reflect the energy level alignment at the organic/metal buried interface.^[20] Moreover, specific processing condition employed to fabricate the sample for direct energy level study may differ from those adopted for actual device fabrication.^[21] Because there is no direct techniques to measure the EWF of the buried interface,^[22] the effect of the self-generated interlayers is evaluated in this study from the device performance. The bottom-gate top-contact OFETs in this study are fabricated in staggered device configuration on silicon wafers with a thermal oxide dielectric and top evaporated Ag (or Au) source and drain contacts, as shown in Figure 1(a). In this configuration, charge injection/extraction extends over the large overlap region between the source–drain and gate electrodes ^[23] effectively increasing the contact area. This device structure augments the contribution of additives to contact resistance and subsequent device performance and it can be assessed by the saturation mobility (μ_{Sat}). μ_{Sat} is calculated using equation (1).

$$\mu_{Sat} = \frac{2L(\frac{\sqrt{I_{Drain}}}{V_{Gate} - V_{Threshold}})^2}{WC} \quad (1)$$

Where, W, L and C are the transistor channel width, channel length and capacitance of the gate insulator per unit area, respectively. I_{Drain} , V_{Gate} and $V_{Threshold}$ are the measured drain-to-source current, gate-to-source voltage and threshold voltage measured from the transfer characteristics, respectively.^[24] An optical image of a one OFET device is shown in Figure 1(b), and a substrate containing 20 devices with different channel lengths but similar channel width is shown in the inset.

To study the effect of top self-generated interlayers on contact resistance in p- and n-type OFETs we selected two additives: HEG-DT and 4-FM, and two semiconducting polymers: p-type DPP-T-TT and n-type P(NDI2OD-T2), shown in Figure 1(c)-(f). The surface energy of

both additives, HEG-DT ($\sim 55 \text{ mJ m}^{-1}$)^[14a] and 4-FM ($\sim 35.7 \text{ mJ m}^{-2}$),^{[22] [25]} are higher than those of both polymers, DPP-T-TT ($\sim 33.16 \text{ mJ m}^{-2}$)^[26] and P(NDI2OD-T2) ($\sim 23.7 \text{ mJ m}^{-2}$),^[27] therefore the additives are not expected to enrich the air/blend surface of the spun films. Because both additives have similar methane-thiol end-groups, the bond-dipole formed between the thiol and Ag is the same for both molecules. However, the significantly different backbones can impose different effects on the EWF. HEG-DT, with the polar O-C bonds, is known to reduce the EWF at Ag electrode interfaces,^[13a, 14a] in contrast, fluorinated aromatic thiol molecules, such as 4-FM, are known to increase the EWF.^[13b, 28] First, we studied the effect of 4-FM and HEG-DT additives on p-type DPP-T-TT OFETs, as shown in Figure 2-(a)-(c). The overall statistical yield of DPP-T-TT based device performance is shown in Figure S1 (a) (b) (c) (ESI[†]). The HOMO and LUMO level of this polymer are 5.3 eV and 4.07 eV, respectively.^[29] Hence, in p-type device operation an Ag electrode (average work function $4.7 \pm 0.2 \text{ eV}$)^[7, 13b, 18] imposes a high energy barrier for hole injection into the polymer's HOMO level. The output characteristics, Figure 2(a), and transfer characteristics, green line in Figure 2(d), of a pristine DPP-T-TT device (no additive) show a saturation hole mobility of $0.2 \pm 0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and threshold voltage of -6.5V at drain-source voltage of -20V (averaged over 5 devices). This mobility value is comparable with previously reported studies.^[30] The small V-shaped transfer curve (green line in Figure 2-(d)) is representative of the ambipolar nature of this polymer.^[29] As expected, the device suffers significant contact resistance which is manifested in the S-shape suppression of the drain current (I_{Drain}) at low source-drain voltages (V_{Drain}), shown in the inset of Figure 2-(a).

Mixing the 4-FM additive in the DPP-T-TT active layer leads to an overall increase of the I_{Drain} , by about a factor of 5, and a noticeable reduction of the contact resistance, as can be seen in Figure 2-(b) and its inset. The extracted saturation mobility increased to $0.55 \pm 0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (averaged over 8 devices). This enhancement of OFET device performance is comparable to

the reported traditional SAM-induced increase of EWF and its associated reduction of the hole-injection barrier.^[6b, 31] We point out that the threshold voltage shifts from -6.5V to -5V, indicating additional accumulation of holes due to the reduction in contact resistance. Although this could be attribute to bulk doping of the semiconductor, we rule out this possibility as we see no increase in off-current.

The HEG-DT additive has a completely different effect on DPP-T-TT p-type OFETs. Figure 2-(c) shows that mixing HEG-DT in the DPP-T-TT active layer dramatically reduces the I_{Drain} , saturation mobility $0.06 \pm 0.01 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$ (averaged over 6 devices), and strongly suppresses the I_{Drain} at low V_{Drain} (Figure 2(c) inset), effectively increasing the contact resistance. The negative effect of the HEG-DT interlayer on the device characteristic is also evident from the further reduction of the threshold voltage to -10.7V, and the more prominent V-shaped transfer curve (Figure 2(d)). This result is in good agreement with the previously shown effect of HEG-DT on OSC, associated with a reduction of the EWF by the self-generated HEG-DT interlayer.^[14a] Based on these device performances we suggest that a self-generated 4-FM interlayer increases the EWF at the polymer/Ag interface effectively reducing the contact resistance and allowing more efficient hole-injection into the polymer; in contrast, a self-generated HEG-DT interlayer reduces the EWF at the polymer/Ag interface effectively increasing the contact resistance and stalling hole-injection into the polymer.

The transmission line method (TLM) was employed to quantitatively evaluate the effects of 4-FM and HEG-DT on OFETs. Figure S2 of the supplementary information (ESI†) shows the width-normalized device resistance ($R \cdot W$ for $W=1000\mu\text{m}$) of the DPP-T-TT OFETs without or with additives, with respect to the channel lengths (30 μm , 40 μm , 50 μm , and 80 μm) at gate-source voltage of -20V. The width-normalized contact resistances ($R_c \cdot W$), extracted from the y-intercept, are listed in table S1 (ESI†). The variation of width-normalized contact resistance with respect to gate voltage (V_{Gate}), shown in Figure 2-(e), unambiguously confirms that the

contact resistance for the device with 4-FM is much lower than that of the pristine device; and the device with HEG-DT shows very high contact resistance.^[11, 32] This is further supported by differential linear-region field-effect mobility as a function of gate-source voltage calculated (using equation Seq-1 ESI†) for OFET devices with and without additives as shown in Figure 2-(f). For the pristine DPP-T-TT device (green line), maximum linear region field-effect mobility is about $0.033 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$, almost one order of magnitude smaller than the measured saturation field-effect mobility. The large discrepancy in field-effect mobility for the two regions of the device operation results from poor charge injection due to high contact resistance.^[33] For the OFET device with 4-FM, the maximum linear region field-effect mobility was about $0.25 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$. This value is closer to the measured saturation field-effect mobility for the same devices indicating substantially improved charge carrier injection associated with the 4-FM interlayer.

We speculate that the overall contact resistance reduction by 4-FM depends on the coverage area of the polymer/Ag interface by 4-FM molecules. Under such conditions, the concentration of 4-FM molecules mixed in the active layer should be optimized to yield a full and continuous interlayer. To do so we studied the evolution of the contact resistance with the concentration of 4-FM molecules in the polymer solution. Figure 3(a) shows the linear region of the transfer characteristics, highly affected by the contact resistance, of OFETs with different concentrations of 4-FM. Apparently, the drain current increases semi-linearly by an order of magnitude with increasing 4-FM concentration up to 2mg/ml concentration, while the turn-on voltage is reduced. Reduction in turn on voltage along with increasing drain current indicates a reduction in the charge injection barrier. The TLM results, Figure 4(b), are in good agreement with this conclusion showing a gradual reduction in the width normalized contact resistance with 4-FM concentration. For the pristine device, the width normalized contact resistance is 96 k Ω .cm, and adding 0.75mg/ml, 1.5mg/ml and 2mg/ml 4-FM devices reduces it to 69.5, 25 and

7.2 k Ω .cm, respectively. It clearly indicates 4-FM reduces the DPP-T-TT/Ag contact resistance which is close to the previously reported DPP-T-TT/Au contact resistance.^[34] However, further increase in 4-FM concentration increases the contact resistance and deteriorates device performance probably because once a continuous 4-FM interlayer is formed there is no longer a driving force for migration and excess 4-FM molecules linger in the bulk film effectively increasing the resistance.

After studying the effect of HEG-DT and 4-FM on p-type OFETs we implemented the same additives in n-type P(NDI2OD-T2) OFETs. In these devices, the injection barrier for electrons is determined by the difference between the metal's work function and the LUMO level of the organic semiconductor. The LUMO level of P(NDI2OD-T2), a high mobility n-type polymer, is at 3.84 eV,^[35] effectively imposing a ~ 0.86 eV barrier for electron injection from Ag electrodes (estimated from the Mott-Schottky model). Figure 4 (a) (b) (c) show the output characteristics of the n-type OFETs without and with 4-FM or HEG-DT additives blended into the active layer, respectively. The overall statistical yield of P(NDI2OD-T2) based device performance is shown in Figure S1 (d) (e) (f) (ESI[†]). The pristine device shows electron mobility of 0.02 ± 0.01 cm² V⁻¹s⁻¹ (averaged over 6 devices) and a significant drain current depression in low drain-source voltages revealing the high contact resistance. Similar to the p-type device presented in Figure 2, the n-type OFETs device performances also varies considerably after introducing the additives into the active layer. With 4-FM the electron mobility is significantly reduced, to 0.006 ± 0.002 cm² V⁻¹s⁻¹ (averaged over 4 devices), reflecting a high contact barrier. On the other hand, with HEG-DT the drain-source on-current and mobility are more than doubled (averaged over 6 devices). As a result of the change in the electron injection barrier the turn-on voltage of the device without additives is 5V and shifts to 8.5V and 2.5V with 4-FM and HEG-DT additives, respectively. The n-channel transistor parameters are summarized in table S2 (ESI[†]).

The transfer curve in Figure 4-(d) reveals that the pristine device shows ambipolar behavior and exhibits V-shaped transfer curve with poor electron injection. With the HEG-DT additive the device exhibits a linear increase in drain current at low drain voltages, suggesting Ohmic electron injection. In contrast, the 4-FM additive increases the EWF and the energy barrier for electron injection but reduces the barrier for hole injection, effectively enhancing the hole current in the device. Figure 4-(e) clearly shows the enhancement of p-type performance by 4-FM from the significant increase of I_{Drain} and the noticeable reduction of the S-shape at low drain-source voltages. The linear region field effect mobility peak for the pristine device, shown in Figure 4-(f), indicates a pronounced dependence of contact resistance on the gate bias.^[32] For this pristine device the maximum linear region field effect mobility is one order of magnitude smaller than the saturation mobility. However, for the device with HEG-DT the mobility measured in linear region is surprisingly identical to that calculated from the saturation region, which corroborates the strong reduction of contact resistance and significant improved charge carrier injection by HEG-DT.

Finally, we use electron microscopy and X-ray photoemission spectroscopy to corroborate the formation of self-generated interlayers that determine the device performances. Because 4-FM is the only fluorine-containing species in the system, we use cross section Scanning Transmission Electron Microscopy (STEM) elemental mapping of fluorine to determine its location and distribution in the device. For HEG-DT we use its unique (XPS) fingerprint, the C-O bond, to study its migration in the active layer before and after Ag deposition. Figure 5-(a) shows the top-view schematic illustration and High-angle annular dark-field (HAADF) cross-section image of a device with 4-FM. The image clearly shows the semiconducting polymer film (black contrast) sandwiched between the bottom SiO_2 dielectric (dark gray contrast) and top Ag contact (bright contrast). The noticeable top conductive layers of graphite and Pt (bright contrast) were deposited during sample preparation to avoid damage by the ion beam. Figure 5

(b) and (c) show a HADDF-STEM image and corresponding schematic illustration of a section of (a), respectively. STEM-EDX elemental mapping and quantitative graphical representation of the concentrations of carbon, Ag and fluorine in the same section are shown in Figure 5-(c)-(f), respectively. The elemental maps show nearly no fluorine signal counts in the polymer layer, but a noticeable signal associated with the Ag signal. In Figure S3 (ESI[†]), the atomic fraction informaton, which gives the percentage of one kind of atom relative to the total number of atoms, has been plotted with respect to position for all primary elements present in the sample. The absence of fluorine atom in the polymer layer indicates that although 4-FM was initially deposited with the polymer, it migrated during processing to the Ag contact. Because the surface energy of 4-FM is higher than that of the polymers, as mentioned above, it does not enrich the film surface after spin coating. Therefore, we suggest that strong interactions between Ag and the thiol end-group of 4-FM molecules induce the migration of 4-FM to Ag during metal deposition. This migration results in formation of a 4-FM interlayer between the polymer and the Ag electrodes following the mechanism described in the introduction section. This self-generated interlayer modulates the EWF at the polymer/Ag interfaces significantly affecting the contact resistance and overall device performance.

Studying the migration of HEG-DT to the Ag/polymer interface by XPS fully confirms the suggested mechanism for additive migration and interlayer generation. We performed XPS measurements on bare and Ag-covered regions of DPP-T-TT polymer films with and without HEG-DT, as schematically shown in the insets of Figure 6. The Ag layer was thin enough (3nm) so that the chemical composition of the buried polymer/Ag interfaces can be analyzed and compared to the adjacent bare area.^[14c] Note that the sample temperature was kept under 30°C, with no additional annealing processes afterwards. Figure 6 shows the bare-area (blue circles) and Ag-covered (red circles) XPS spectra of DPP-T-TT films without (Figure 6a) and with HEG-DT (Figure 6b). The XPS spectra of the bare polymer surfaces without or with HEG-DT

show a main C 1s peak at 285 eV, characteristic of C–C/C–H bonds of the polymer. There is no evidence of the HEG-DT characteristic C–O bond, expected at 286.45 eV, at the polymer/air interface.^[36] This result is in agreement with the unfavorable surface enrichment of the film by the high surface energy additive component. Hence, we conclude that HEG-DT additive molecules do not migrate to the film surface during spin coating and most likely accumulate at the bottom substrate/polymer interface due to its high surface energy.

Next, we use XPS to analyze the composition of polymer/Ag interfaces in films processed without and with HEG-DT (red circles in Figure 5 (a), (b), respectively). The XPS spectra of pristine DPP-T-TT/Ag interface (red circles Figure 5(a)) is similar to that of the adjacent DPP-T-TT/air interface (blue circles Figure 5(a)). In contrast, the XPS C 1s spectra of the Ag-covered DPP-T-TT film processed with HEG-DT additive molecules (red circles Figure 5 (b)) shows a new shoulder centered at 286.6 eV. This peak is associated with C–O bonds and is the figure-print of HEG-DT. Hence, we conclude that HEG-DT additive molecules migrate to the film surface during Ag deposition due to strong interactions between Ag and the thiol end-group of HEG-DT molecules. This migration results in formation of a HEG-DT interlayer between the polymer and the Ag electrodes following the mechanism described in the introduction section. We suggest that the HEG-DT self-generated interlayers modulate the EWF at the polymer/Ag interfaces significantly affecting the contact resistance and overall device performance.

Finally, to demonstrate the versatility and generality of self-generated interlayers for modulating contact resistance in OFETs we also fabricated DPP-T-TT OFETs with HEG-DT and 4-FM additives and Au electrodes. Because both additives are thiol-terminated they are expected to also migrate to Au contacts and modulate the EWF in a similar manner to that observed for corresponding DPP-T-TT OFETs with Ag contacts. Indeed, the transfer characteristics of the Au OFETs, supplementary information section Figure S4-(a) (ESI[†]), show that 4-FM improves hole injection into DPP-T-TT while HEG-DT suppresses it, in good

agreement with the performances of the devices with Ag contacts shown in Figure 2. The contribution of 4-FM to the polymer/Au interface is not as significant as that observed for the polymer/Ag interface because the work function of Au is higher than that of Ag and hence the barrier for hole injection from Au to the HOMO of DPP-T-TT is lower than that from Ag. In both Au and Ag devices, however, HEG-DT dramatically suppresses hole-injection and deteriorates device performance. XPS spectra of organic/air and organic/Au interfaces of DPP-T-TT films processed with HEG-DT additive molecules are also shown in the supplementary information section (Figure S4-b). Presence of the C-O 286.6 eV peak at the organic/Au interface confirms migration of HEG-DT to the polymer/Au interface. It is also important to note that the absorption spectra and X-ray diffraction patterns of DPP-T-TT films without and with additives are identical, supplementary information section Figure S5 (ESI[†]), confirming that the additives affect the interfaces and hence contact resistance, but have little to no effect on bulk morphology and crystallinity. This is in contrast to other studies that use solvent additives to deliberately modify the structure of the bulk film.^[37]

3. Summary and Conclusions

In summary, we demonstrated a simple, versatile, self-generating and self-limiting methodology for processing interlayers in OFETs induced by additive-metal interactions. Using DPP-T-TT and P(NDI2OD-T2) based OFETs as a research platform, we showed that electron and hole injection can be tuned by blending judiciously-selected additives in the polymer film. Strong affinity between the end-group of the additive and the depositing top metal contact induces additive migration to the polymer/metal interface to form a continuous interlayer. Presence of the interlayer and suggested mechanism were corroborated by STEM and XPS. The effect of self-generated interlayers on the electrical performance of the p- and n-type OFETs was investigated in terms of the electron field-effect mobility (μ_{FET}), turn-on voltage (V_{ON}) and

contact resistance (R_C). The results indicate that self-generated interlayers can tune the effective work function at buried metal-organic interfaces and modulate the charge carrier injection. This interlayer-generation methodology reduces the number of fabrication stages and is a step towards cheap, simple and roll-to-roll processing of low-cost, large area organic electronic applications, and is compatible with fully flexible, printed CMOS-like integrated circuits.

4. Experimental

Materials: DPP-T-TT ($M_w = 75,000 \text{ g mol}^{-1}$) was purchased from 1-Material Inc and PNDI(2OD)2T ($M_w = 289,730 \text{ g mol}^{-1}$) was purchased from Ossila Limited. 4-FM ($M_w = 142.195 \text{ g mol}^{-1}$), HEG-DT ($M_w = 314.5 \text{ g mol}^{-1}$) and Trichloro(octadecyl)silane ($M_w = 387.93 \text{ g mol}^{-1}$) were purchased from Sigma Aldrich. All materials were used as received. Heavily p-doped silicon wafers with a 200nm SiO₂ dielectric layer were purchased from University Wafer Inc.

Device fabrication: Si-substrates were cleaned by sonication in acetone for 5 min, then immersed in piranha solution for 20 min at 100°C and several times in distilled water. Finally, substrates were washed by 2-propanol for 10min in sonication. The cleaned substrates were treated by Trichloro(octadecyl) silane (OTS) in a vacuum oven at 90°C for 30 min. OTS treated substrates were cleaned two times in toluene and one time in 2-propanol, separately, for 5 min each and dried by nitrogen. 1,2-Dichlorobenzene solutions of DPP-T-TT (12 mg/mL), PNDI(2OD)2T (12 mg/mL), 4-FM (14 mg/mL or 100mM) and HEG-DT (8mg/ml) were prepared and mixed to obtain: DPP-T-TT:4-FM solutions of 10:0 (reference), 10:0.75, 10:1.4, 10:2; 10:2.85 mg/mL; PNDI(2OD)2T:4-FM solution of 10:2 mg/ml; and DPP-T-TT:HEG-DT

and PNDI(2OD)2T:HEG-DT 10:1.5 mg/ml solutions. All active semiconducting layers were deposited by spin-coating at 1500 rpm for 140second. The spin-coated films were dried for one hour in a vacuum chamber at room temperature. Finally, 100 nm-thick silver or gold electrodes were deposited through a shadow mask using a thermal evaporator at a deposition rate of $5 \text{ \AA s}^{-1}$ under 5×10^{-6} Torr at room temperature for the source/drain electrodes of the OFETs. For each type, 20×2 OFETs were prepared with four different channel lengths: 30, 40, 50, 60 and $80 \mu\text{m}$ with ± 5 tolerance (5 devices of each channel length). All presented curves are average performances over at least four similar devices.

Characterization

Themis-TEM: Cross-section specimens for High Resolution Transmission Electron Microscopy (HRTEM) studies were prepared using a dual-beam Focused Ion Beam (FIB) microscope (FEI Helios NanoLab DualBeam G3 UC). HRTEM analysis was conducted in a monochromated and aberration corrected TEM (FEI Titan Cubed Themis G2 300) using tension voltage of 300 KeV. Chemical analysis of the layers was conducted using EDS in High Angle Annular Dark Field (HAADF) Scanning Transmission Electron Microscopy (STEM) mode.

X-Ray photoelectron spectroscopy (XPS): X-ray Photoelectron Spectroscopy (XPS) measurements were performed in UHV (2.5×10^{-10} Torr base pressure) using 5600 Multi-Technique System (PHI, USA). The sample was irradiated with an Al K_{α} monochromatic source (1486.6 eV) and the emitted electrons were analyzed with a Spherical Capacitor Analyzer using a slit aperture of 0.8 mm in diameter. Line-shape analysis was done using the XPSPEAK 4.1 software after a Shirley-type background subtraction. The binding energy scale calibration of the C1s spectra was done by referencing the C–C/C–H binding signal to 285 eV.

X-Ray Diffraction (XRD): Grazing-incidence X-ray diffraction (GIXRD) measurements of films on silicon substrates were conducted on a D/MAX-2500 series RIGAKU system with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The measurements were obtained in a 2θ scanning interval between 3° and 25° .

UV-VIS spectroscopy: Optical absorbance measurements of films on quartz were performed using a Varian Cary 100 scan UV–vis spectrophotometer.

Device characterization: Device characterization was performed inside glovebox nitrogen atmosphere under dark condition using a Keithley 2612B dual source-meter. Test Script Builder (TSB) automated software was used for data acquisition of the I–V output.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

We thank to Dr. Amit Sharma from Material science and engineering department of the Technion for helpful discussions. This research was supported by a grant from European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No 675867.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

References

- [1] a) Y. Xu, C. Liu, D. Khim, Y.-Y. Noh, *Physical Chemistry Chemical Physics* **2015**, 17, 26553; b) H. Sirringhaus, *Advanced Materials* **2005**, 17, 2411; c) M. Nikolka, I. Nasrallah, B. Rose, M. K. Ravva, K. Broch, A. Sadhanala, D. Harkin, J. Charmet, M. Hurhangee, A. Brown, S. Illig, P. Too, J. Jongman, I. McCulloch, J.-L. Bredas, H.

- Sirringhaus, *Nature materials* **2017**, 16, 356; d) S. H. Ko, H. Pan, C. P. Grigoropoulos, C. K. Luscombe, J. M. J. Fréchet, D. Poulikakos, *Nanotechnology* **2007**, 18, 345202; e) B. Kang, N. Park, H. Min, J. Lee, H. Jeong, S. Baek, K. Cho, H. S. Lee, *Advanced Electronic Materials* **2015**, 1; f) S. Allard, M. Forster, B. Souhace, H. Thiem, U. Scherf, *Angewandte Chemie International Edition* **2008**, 47, 4070.
- [2] a) C. Shuoran, S. Meng, Z. Cong, G. Meng, B. Bin, Y. Qiang, S. Bin, S. Yanlin, *Advanced Materials* **2015**, 27, 3928; b) E. Ralph, A. Milan, R. Tobias, S. Philip, L. Uli, H. S. Gerardo, *Advanced Materials* **2016**, 28, 7708; c) Y. L. Kong, I. A. Tamargo, H. Kim, B. N. Johnson, M. K. Gupta, T.-W. Koh, H.-A. Chin, D. A. Steingart, B. P. Rand, M. C. McAlpine, *Nano Letters* **2014**, 14, 7017; d) V. A. D., B. T. A., B. J. William, R. J. R., C. Alex, K. Arda, B. J. Daniel, D. M. F., L. J. A., *Advanced Materials* **2017**, 29, 1703817; e) Z. Zhichao, R. Xiaochen, P. Boyu, W. Zongrong, W. Xinyu, P. Ke, S. Bowen, M. Qian, C. P. K. L., *Advanced Functional Materials* **2015**, 25, 6112.
- [3] a) D. Venkateshvaran, M. Nikolka, A. Sadhanala, V. Lemaure, M. Zelazny, M. Kepa, M. Hurhangee, A. J. Kronemeijer, V. Pecunia, I. Nasrallah, I. Romanov, K. Broch, I. McCulloch, D. Emin, Y. Olivier, J. Cornil, D. Beljonne, H. Sirringhaus, *Nature* **2014**, 515, 384; b) R. S. Ashraf, I. Meager, M. Nikolka, M. Kirkus, M. Planells, B. C. Schroeder, S. Holliday, M. Hurhangee, C. B. Nielsen, H. Sirringhaus, I. McCulloch, *Journal of the American Chemical Society* **2015**, 137, 1314.
- [4] a) J. Veres, S. D. Ogier, S. W. Leeming, D. C. Cupertino, S. M. Khaffaf, *Advanced Functional Materials* **2003**, 13, 199; b) L. A. Majewski, R. Schroeder, M. Grell, *Advanced Functional Materials* **2005**, 15, 1017; c) V. Raghuwanshi, D. Bharti, S. P. Tiwari, *Organic Electronics* **2016**, 31, 177.
- [5] a) K. Fukuda, Y. Takeda, Y. Yoshimura, R. Shiwaku, L. T. Tran, T. Sekine, M. Mizukami, D. Kumaki, S. Tokito, *Nat Commun* **2014**, 5; b) J. Krantz, K. Forberich, P. Kubis, F. Machui, J. Min, T. Stubhan, C. J. Brabec, *Organic Electronics* **2015**, 17, 334.
- [6] a) S. Choi, C. Fuentes-Hernandez, C.-Y. Wang, T. M. Khan, F. A. Larrain, Y. Zhang, S. Barlow, S. R. Marder, B. Kippelen, *ACS applied materials & interfaces* **2016**, 8, 24744; b) J. Roh, T. Lee, C.-m. Kang, J. Kwak, P. Lang, G. Horowitz, H. Kim, C. Lee, *Scientific Reports* **7**, 46365.
- [7] J. Kim, Y. S. Rim, Y. Liu, A. C. Serino, J. C. Thomas, H. Chen, Y. Yang, P. S. Weiss, *Nano letters* **2014**, 14, 2946.
- [8] a) T. Mori, T. Kozawa, T. Ohwaki, Y. Taga, S. Nagai, S. Yamasaki, S. Asami, N. Shibata, M. Koike, *Applied Physics Letters* **2010**, 69, 3537; b) S. Chuang, C. Battaglia, A. Azcatl, S. McDonnell, J. S. Kang, X. Yin, M. Tosun, R. Kapadia, H. Fang, R. M. Wallace, A. Javey, *Nano letters* **2014**, 14, 1337.
- [9] S. Braun, W. R. Salaneck, M. Fahlman, *Advanced Materials* **2009**, 21, 1450.
- [10] B. de Boer, A. Hadipour, M. M. Mandoc, T. van Woudenberg, P. W. M. Blom, *Advanced Materials* **2005**, 17, 621.
- [11] M. Kano, T. Minari, K. Tsukagoshi, *Applied Physics Letters* **2009**, 94, 143304.
- [12] Y.-M. Chang, C.-Y. Leu, *Journal of Materials Chemistry A* **2013**, 1, 6446.
- [13] a) Y. Zhou, C. Fuentes-Hernandez, J. Shim, J. Meyer, A. J. Giordano, H. Li, P. Winget, T. Papadopoulos, H. Cheun, J. Kim, M. Fenoll, A. Dindar, W. Haske, E. Najafabadi, T. M. Khan, H. Sojoudi, S. Barlow, S. Graham, J.-L. Brédas, S. R. Marder, A. Kahn, B. Kippelen, *Science (New York, N.Y.)* **2012**, 336, 327; b) J.-P. Hong, A.-Y. Park, S. Lee, J. Kang, N. Shin, D. Y. Yoon, *Applied Physics Letters* **2008**, 92, 143311.
- [14] a) B. Shamieh, S. Obuchovsky, G. L. Frey, *Journal of Materials Chemistry C* **2016**, 4, 1821; b) I. Deckman, M. Moshonov, S. Obuchovsky, R. Brenner, G. L. Frey, *Journal of*

- Materials Chemistry A* **2014**, 2, 16746; c) I. Dekman, R. Brener, G. L. Frey, *Journal of Materials Chemistry C* **2013**, 1, 6522; d) L. Nouzman, G. L. Frey, *Journal of Materials Chemistry C* **2017**, 5, 12744; e) J. Vinokur, S. Obuchovsky, I. Deckman, L. Shoham, T. Mates, M. L. Chabinye, G. L. Frey, *ACS applied materials & interfaces* **2017**, 9, 29889.
- [15] J. Vinokur, I. Deckman, T. Sarkar, L. Nouzman, B. Shamieh, G. L. Frey, *Advanced Materials* **2018**, 30, 1706803.
- [16] a) V. A. Kolesov, C. Fuentes-Hernandez, W.-F. Chou, N. Aizawa, F. A. Larrain, M. Wang, A. Perrotta, S. Choi, S. Graham, G. C. Bazan, T.-Q. Nguyen, S. R. Marder, B. Kippelen, *Nature Materials* **2016**, 16, 474; b) L. Li, L. Xiao, H. Qin, K. Gao, J. Peng, Y. Cao, F. Liu, T. P. Russell, X. Peng, *ACS Applied Materials & Interfaces* **2015**, 7, 21495.
- [17] J. Razzell-Hollis, W. C. Tsoi, J.-S. Kim, *Journal of Materials Chemistry C* **2013**, 1, 6235.
- [18] S. Choi, F. A. Larrain, C.-Y. Wang, C. Fuentes-Hernandez, W.-F. Chou, B. Kippelen, *Journal of Materials Chemistry C* **2016**, 4, 8297.
- [19] E. L. Ratcliff, B. Zacher, N. R. Armstrong, *The journal of physical chemistry letters* **2011**, 2, 1337.
- [20] B. Shamieh, A. S. Anselmo, U. Vogel, E. Lariou, S. C. Hayes, N. Koch, G. L. Frey, *Journal of Materials Chemistry C* **2018**, 6, 8060.
- [21] A. Guerrero, B. Dörling, T. Ripolles-Sanchis, M. Aghamohammadi, E. Barrena, M. Campoy-Quiles, G. Garcia-Belmonte, *ACS Nano* **2013**, 7, 4637.
- [22] Y.-J. Yu, Y. Zhao, S. Ryu, L. E. Brus, K. S. Kim, P. Kim, *Nano Letters* **2009**, 9, 3430.
- [23] R. A. Street, A. Salleo, *Applied Physics Letters* **2002**, 81, 2887.
- [24] a) E. Fortunato, P. Barquinha, R. Martins, *Advanced Materials* **2012**, 24, 2945; b) A. C. Tickle.
- [25] R. S. o. Chemistry, 4-Fluoro benzyl mercaptan | C₇H₇FS | ChemSpider, <http://www.chemspider.com/Chemical-Structure.76811.html>, accessed: 2018, July 10
- [26] J. Xu, S. Wang, G.-J. N. Wang, C. Zhu, S. Luo, L. Jin, X. Gu, S. Chen, V. R. Feig, J. W. F. To, S. Rondeau-Gagné, J. Park, B. C. Schroeder, C. Lu, J. Y. Oh, Y. Wang, Y.-H. Kim, H. Yan, R. Sinclair, D. Zhou, G. Xue, B. Murmann, C. Linder, W. Cai, J. B.-H. Tok, J. W. Chung, Z. Bao, *Science* **2017**, 355, 59.
- [27] S. Fabiano, S. Himmelberger, M. Drees, Z. Chen, R. M. Altamimi, A. Salleo, M. A. Loi, A. Facchetti, *Advanced Energy Materials* **2014**, 4.
- [28] S. Tatara, Y. Kuzumoto, M. Kitamura, *Japanese Journal of Applied Physics* **2016**, 55, 03DD02.
- [29] D. X. Long, K. J. Baeg, Y. Xu, S. J. Kang, M. G. Kim, G. W. Lee, Y. Y. Noh, *Advanced Functional Materials* **2014**, 24, 6484.
- [30] Y. Hu, G. Li, W. Peng, Z. Chen, *IEEE Electron Device Letters* **2018**, 39, 421.
- [31] X. Cheng, Y. Y. Noh, J. Wang, M. Tello, J. Frisch, R. P. Blum, A. Vollmer, J. P. Rabe, N. Koch, H. Sirringhaus, *Advanced Functional Materials* **2009**, 19, 2407.
- [32] E. G. Bittle, J. I. Basham, T. N. Jackson, O. D. Jurchescu, D. J. Gundlach, *Nat Commun* **7**, 10908.
- [33] D. J. Gundlach, L. L. Jia, T. N. Jackson, *IEEE Electron Device Letters* **2001**, 22, 571.
- [34] M. D. Mamo, E.-S. Shin, Y.-Y. Noh, *Journal of Materials Chemistry C* **2017**, 5, 10900.
- [35] L. Gao, Z.-G. Zhang, L. Xue, J. Min, J. Zhang, Z. Wei, Y. Li, *Advanced materials (Deerfield Beach, Fla.)* **2016**, 28, 1884.
- [36] *Journal of Chemical Education* **1993**, 70, A25.
- [37] a) J. W. Jeong, G. Jo, S. Choi, Y. A. Kim, H. Yoon, S.-W. Ryu, J. Jung, M. Chang, *ACS Applied Materials & Interfaces* **2018**, 10, 18131; b) G. J. Chae, S.-H. Jeong, J. H.

Baek, B. Walker, C. K. Song, J. H. Seo, *Journal of Materials Chemistry C* **2013**, 1, 4216.

Figure 1: Device schematics and chemical structures of the materials used in this study: (a) device architecture of bottom-gate top-contact OFET; (b) An optical image of one OFET device ($W/L=1000/30$), and a substrate containing 20 devices with different channel lengths: $L=30$

μm , 40 μm , 50 μm , and 80 μm , $W=1000 \mu\text{m}$ (Inset). (c) HEG-DT additive, (d) 4-FM additive; (e) p-type DPP-T-TT, (f) n-type P(NDI2OD-T2).

Figure 2: Output and transfer characteristics of p-type DPP-T-TT OFETs with contact resistance and linear region field-effect mobility comparisons. Output characteristics of (a) pristine, (b) with 4-FM and (c) with HEG-DT devices with channel length 30 μm and channel width 1000 μm at $V_{\text{Gate}} = 0, -10$ and -20 V . Insets show the linear region ($V_{\text{Drain}} : 2.5$ to -5 V) output characteristics. (d) Transfer characteristics of OFETs of the same devices with and without the additives. Dashed lines represent the gate current (I_{Gate}) to the corresponding devices. (e) Comparison of width-normalized contact resistance of the OFETs at $V_{\text{Gate}} = -10, -20$ and -30 V extracted by TLM. (f) Comparison of so-called Linear region field-effect mobility as a function of V_{Gate} , measured from transconductance for the OTFTs biased at V_{Drain} of -1 V .

Figure 3: The effect of 4-FM concentration variation on (a) linear region transfer characteristics and (b) the contact resistance in p-type DPP-T-TT devices (channel length: $30 \mu\text{m}$ and channel width: $1000 \mu\text{m}$), extracted by TLM methods (inset).

Figure 4: Output and transfer characteristics of n-type P(NDI2OD-T2) OFETs with linear region field-effect mobility comparison and p-type P(NDI2OD-T2) OFETs output characteristics. Output characteristics of n-type P(NDI2OD-T2) OFETs: (a) pristine, (b) with

4-FM and (c) with HEG-DT devices with channel length 30 μm and channel width 1000 μm at $V_{\text{Gate}} = 0, -10$ and -20V . Insets show the linear region ($V_{\text{Drain}} : 2.5$ to 5V) out-put characteristics. (d) Transfer characteristics of the same OFETs with and without additives. Dashed lines represent the gate current (I_{Gate}) to the corresponding devices. (e) p-type P(NDI2OD-T2) OFET output characteristics (at $V_{\text{Gate}} : 0, -10, -20$ and -30V) without (bottom) and with 4-FM additive. (f) Comparison of the linear region field-effect mobility as a function of V_{Gate} , measured from transconductance for the OTFTs biased at V_{Drain} of 1V .

Figure 5: Cross section electron microscopy imaging and elemental mapping of a DPP-T-TT OFET with 4-FM additive. (a) High-angle annular dark-field (HAADF) cross-section image of a device cross-section. The area of cross section is marked in yellow in the top-view schematic illustration presented in the left corner. The orange rectangle region in (a) marks the area subject to the HAADF-STEM (b) and EDX elemental mapping (d)-(f). (c) is a scheme of the device layers, and (d), (e), (f) are the carbon, silver and fluorine element mapping, respectively. The lines in the images represent quantitative distribution plots of these elements along the cross section.

Figure 6: High-resolution XPS spectra of bare (blue circles) and Ag covered (red circles) DPP-T-TT films without (a) and with (b) HEG-DT additive.

The table of contents:

A study of contact resistance tuning by self-generated interlayer formation in organic field effect transistors. The interlayer material is blended as an additive in the active layer and during metal deposition it migrates to the organic/metal interface. The generated interlayer of additive material modifies the device performance according to the tuning of the contact resistance.

Keyword: organic electronics, self-generated interlayers, organic field effect transistors, TLM

Tanmoy Sarkar, Basel Shamieh, Roy Verbeek, Auke Jisk Kronemeijer, Gerwin Gelinck and Gitti L Frey*

Tuning Contact Resistance in Top-contact *p*- and *n*-type Organic Field Effect Transistors by Self-generated Interlayers

ToC figure:

((Supporting Information can be included here using this template))

Copyright WILEY-VCH Verlag GmbH & Co. KGaA, 69469 Weinheim, Germany, 2016.

Supporting Information

Title: Tuning Contact Resistance in Top-contact *p*- and *n*-type Organic Field Effect Transistors by Self-generated Interlayers

Author(s), and Corresponding Author(s)*: Tanmoy Sarkar, Basel Shamieh, Roy Verbeek, Auke Jisk Kronemeijer, Gerwin Gelinck and Gitti L Frey*

Fig. S1: Statistical analysis of device performances. Mean and standard deviation of the Characteristics of DPP-T-TT devices: (a) pristine, (b) with 4-FM and (c) with HEG-DT. The Mean and standard deviation transfer Characteristics of P(NDI2OD-T2) devcies: (d) pristine, (e) with 4-FM and (f) with HEG-DT devices. The number of each type of devices is shown in each figure.

Fig. S2: Width-normalized device resistance ($R \cdot W$ for $W=1000\mu\text{m}$) of DPP-T-TT OFETs with and without additives, with respect to the channel lengths ($30\mu\text{m}$, $40\mu\text{m}$, $50\mu\text{m}$, and $80\mu\text{m}$) at gate-source voltage of -20V

Table S1: The width-normalized contact resistances ($R_c \cdot W$), extracted from the y-intercept.

Devices	Pristine DPP-T-TT	4-FM+DPP-T-TT	HEG-DT+DPP-T-TT
$R_c W$ [$\text{k}\Omega \cdot \text{cm}$]	96 ± 20	7.2 ± 5	419 ± 80

Equation- Seq-1: Field-effect mobility (μ_{eff}): Obtained by the transconductance (g_m) with low V_{Drain} [1]

$$\mu_{eff} = \frac{g_m}{C_i \frac{W}{L} V_{Drain}}$$

Fig. S3: Atomic fraction information for all primary elements carbon (C), sulphur (S), Silver(Ag) and Fluorine (F) present in sample with respect to the cross section position.

Fig. S4: (a) Transfer characteristics of the DPP-T-TT OFETs with Au contacts with and without additives at $V_{\text{Drain}} = -20\text{V}$. (b) XPS spectra of the bare organic/air and buired organic/Au interfaces of DPP-T-TT films processed with HEG-DT additive molecules.

Table S2: the summary of p- and n- channel transistors with and without additives.

Polymers	Additives	Number of devices	Mobility (cm ² /V·s)	Threshold voltage (V)	Turn-on voltage (V)
DPP-T-TT (p-channel)	Pristine	5	0.2 ±0.05	-6.2	-0.5
	4-FM	8	0.55 ±0.05	-5	0
	HEG-DT	6	0.06 ±0.01	-10.7	-8
P(NDI2OD-T2) (n-channel)	Pristine	6	0.02 ±0.01	9.2	5
	4-FM	4	0.006 ±0.002	18	8.5
	HEG-DT	6	0.05 ±0.002	4.6	2.5

Fig. S5: (a) Absorption spectra and (b) Grazing incidence X-ray diffraction patterns, (inset) intensity and FWHM of (100) diffraction peak of DPP-T-TT films without and with additives.

All absorption spectra and Grazing incidence X-ray diffraction of film with and without the additives are identical indicating that in all films the polymer chains are regularly arranged with highly ordered lamellar planes parallel to the substrate [2]. The (100) diffraction peaks of

pristine and additives mixed ~100nm DPP-T-TT polymer films were observed at $2\theta = 3.9^\circ$, which is attributed to an interplanar distance of 22.6 Å for all kind of polymer films. The identical intensity and full width half maxima (FWHM) of the (100) peak (Figure S5-b) in all samples suggests that incorporating these additives, in the concentrations used in this study, does not affect the structural properties of the bulk polymer film.

References:

- [1] E. Fortunato, P. Barquinha, and R. Martins, "Oxide Semiconductor Thin-Film Transistors: A Review of Recent Advances," *Advanced Materials*, vol. 24, no. 22, pp. 2945–2986, 2012.
- [2] M. Ju Cho *et al.*, "Diketopyrrolopyrrole-based copolymers bearing highly π -extended donating units and their thin-film transistors and photovoltaic cells," *Polymer Chemistry*, vol. 6, no. 1, pp. 150–159, 2015.