

# Polymer Surface Engineering for Efficient Printing of Highly Conductive Metal Nanoparticle Inks

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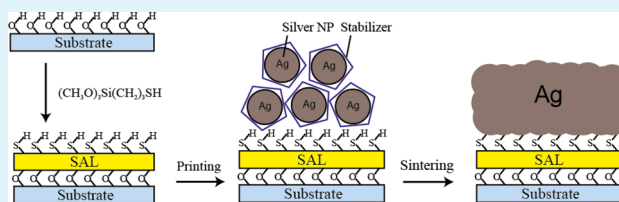
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## S Supporting Information

**ABSTRACT:** An approach to polymer surface modification using self-assembled layers (SALs) of functional alkoxy silanes has been developed in order to improve the printability of silver nanoparticle inks and enhance adhesion between the metal conducting layer and the flexible polymer substrate. The SALs have been fully characterized by AFM, XPS, and WCA, and the resulting printability, adhesion, and electrical conductivity of the screen-printed metal contacts have been estimated by cross-cut

tape test and 4-point probe measurements. It was shown that (3-mercaptopropyl)trimethoxysilane SALs enable significant adhesion improvements for both aqueous- and organic-based silver inks, approaching nearly 100% for PEN and PDMS substrates while exhibiting relatively low sheet resistance up to 0.1  $\Omega$ /sq. It was demonstrated that SALs containing functional  $-\text{SH}$  or  $-\text{NH}_2$  end groups offer the opportunity to increase the affinity of the polymer substrates to silver inks and thus to achieve efficient patterning of highly conductive structures on flexible and stretchable substrates.

**KEYWORDS:** printed electronics, surface modification, self-assembly, functional alkoxy silanes, adhesion enhancement, metal nanoparticle inks



## INTRODUCTION

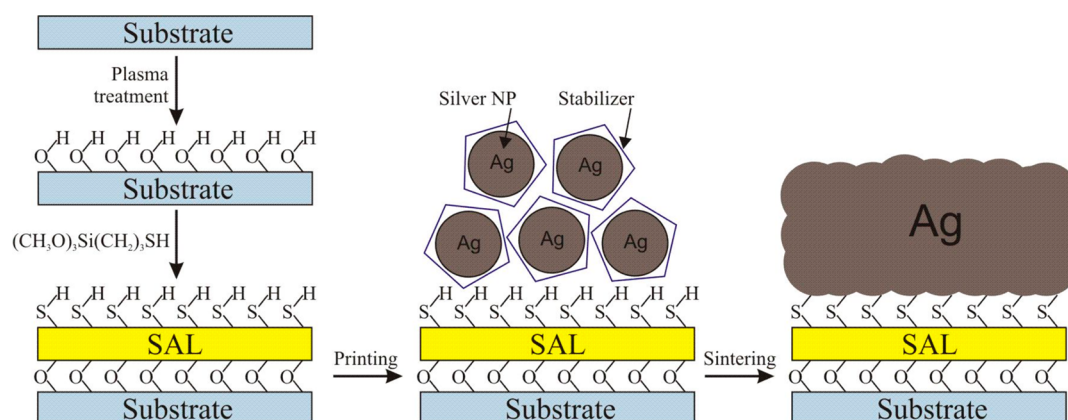
A reliable flexible device is one of the research challenges for the modern electronics industry. Current and emerging examples of devices that can conform to curvilinear surfaces and accommodate large deformations require the ability to manufacture durable functional layers on plastic substrates.<sup>1,2</sup> Printing technologies offer distinct advantages over traditional photolithography methods for addressing this challenge because of their simplicity, high throughput, and low cost.<sup>3,4</sup> For example, metal structures can be cheaply produced by additive direct writing with metal nanoparticle inks onto flexible foils, whereas organic materials are increasingly being used because they are lightweight, more flexible, and less expensive than their inorganic counterparts.<sup>5</sup> Although (semi)conductive and dielectric oligomers and polymers are widely used in organic electronic devices as active layers,<sup>6,7</sup> their application as polymer substrates has shown a number of difficulties.<sup>8,9</sup> The main problem is the low adhesion between the hydrophobic and inert polymer surfaces and the deposited electrically conducting structures, such as metal interconnects and electrodes. The routine printing of metal nanoparticle inks on polymeric surfaces will require the development of new approaches to obtaining proper wetting of the surface and to improving the adhesion of metal nanoparticles to polymer surfaces.

There are two conventional approaches to adhesion improvement: ink modification and substrate conditioning. The most widely used conductive inks for printing contain metal nanoparticles stabilized by surfactants, which form a protective layer on the nanoparticle surface and support uniform distribution of the nanoparticles in the total volume of the ink by preventing agglomeration and sedimentation.<sup>10</sup> In some cases, the surfactants have been shown to play a role in promoting ink adhesion.<sup>11</sup> Silver is a widely used metal in printed electronics because of its low resistivity, affordable cost, and the low melting point of nanoparticles that allows the fabrication of conducting layers on flexible polymer substrates at relatively low temperatures. Different silver nanoparticle inks have been stabilized using either low-molecular-mass surfactants (for example, carboxylate-type) or polymer additives including linear, dendritic, or hyperbranched polymers (polyamides or polyimides) both in water and in organic solvents.<sup>12–15</sup> Though some of the stabilizing agents could be used to improve nanoparticle ink printability on polymer substrates, in practice the stabilizer must be removed before or during the sintering process to enable high conductivity of the deposited structures because if a significant quantity of the

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**Figure 1.** Scheme of the proposed ink adhesion enhancement: (i) polymer substrate modification by plasma treatment, (ii) silanization by MPTS with the formation of SAL, (iii) printing of Ag ink, and (iv) curing of the printed ink.

stabilizers or adhesion promoters remain between nanoparticles within the printed layer then this will decrease the conductivity of the sintered traces. Thus, the identity and pretreatment of the substrate surface can partially compensate for the interference from the nanoparticle stabilization agents, but in practice, the resulting adhesion between the conducting layer and the substrate is usually low for most of the polymer substrates.

Adhesion of inks is improved by substrate conditioning either by physical chemical or chemical modification. The former routinely uses ultraviolet ozone and plasma treatments, including corona discharge, ionized oxygen and high-efficiency plasma<sup>16</sup> to create the following reactive groups on the surface substrate: hydroperoxy, hydroxyl, ether, epoxy, keto, carbonyl, and carboxyl groups. Alternatively, the polymer surface may be treated to improve adhesion by flame treatment, UV irradiation, radio frequency treatment, glow discharge, laser treatment, electron beam treatment, and similar techniques.<sup>17</sup> The main disadvantage of the techniques mentioned above is the short lifetime of the active surface groups, which can be limited to a few hours or even minutes.<sup>17</sup> Some other techniques, such as mechanical treatment or microstructuring,<sup>18</sup> have also been developed; however, they lack versatility and require careful selection of the conditions.

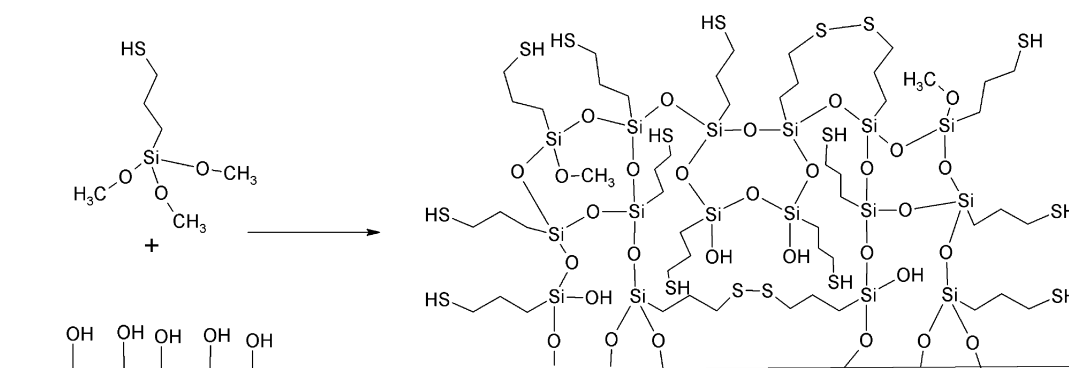
The chemical modification of substrates is usually based on functional molecules that can form self-assembled monolayers (SAMs) or multilayers on the substrate surface that provide covalent, ionic, or hydrogen bonding between the active layer and the substrate.<sup>19</sup> The modification of inorganic and polymer surfaces with monolayers of organic molecules has found widespread application in nanofabrication, sensing, diagnostics, and molecular electronics;<sup>20–26</sup> for example, an SAM was successfully used to enhance interfacial adhesion between copper and silicon substrates.<sup>27</sup> Generally, molecules that are capable of forming an SAM consist of an anchor group, which attaches to the substrate, a tail group, which is responsible for the interactions between the SAM and the media, and a flexible aliphatic spacer, which connects these two groups and promotes the self-assembly processes. Within this general architecture, different chemistries can be combined to build functional molecules.<sup>28</sup> A number of different chemical reactions and deposition approaches are used for surface modification by an SAM. For example, deposition of SAMs of octadecyltrimethoxysilane (OTMS) and octadecyltrichlorosilane (OTS) by a spin-casting technique onto Si/SiO<sub>2</sub> substrates

led to a successful OFET performance improvement,<sup>29</sup> whereas alternatively, the Langmuir–Blodgett technique was employed for SAM formation using OTS.<sup>30</sup>

In this paper, we describe an approach to improve the printability of silver nanoparticle inks on flexible polymer substrates and enhance adhesion between a silver metal conductive layer and a polymer by its surface modification with oxygen-plasma treatment followed by the treatment with functional alkoxy silanes to form self-assembled layers (SAL). As opposed to SAMs, SALs are multilayers having a thickness in the range of tens to hundreds of nanometers. PDMS and PEN were chosen as polymer substrates because of their widespread usage in different applications associated with flexible electronics.<sup>8</sup> The alkoxy silanes (3-mercaptopropyl)-trimethoxysilane (MPTS) and (3-aminopropyl)-trimethoxysilane (APTS) were used as adhesion promoters for silver inks, where trimethoxysilane functional groups can covalently bond to hydroxyl groups formed during plasma treatment on the polymer surface, whereas amino or mercapto functional groups can react with silver particles, displacing stabilizing surfactant from the surface of the nanoparticles. The last process is accompanied by Ag–S bond formation in the case of MPTS or H<sub>2</sub>N/Ag complex formation in the case of APTS. In other words, the functional head and tail groups of the SAL promote the ordered binding of the particles to a surface at the molecular level because of chemical reactions on or close to the surface. This technique improved the printability of silver nanoparticle inks and enhanced the adhesion between the metal conducting layer and the polymer substrate. It was shown that in the case of MPTS on PEN substrates the adhesion was improved from 50 to 100% for water-based Ag nanoparticle ink and from 80 to 95% for organic-based Ag ink. The results for PDMS substrates were even more striking: Their treatment with MPTS led to improvement of the adhesion from 0 to 90% for water-based Ag nanoparticle ink and from 0 to 95% for organic-based Ag ink. The best printed flexible conductor structures generated in this study showed resistivity in the range of 0.09–0.15 Ω/sq, and this showed less than 1% change during bending of the printed structure through a radius of 20 mm. Therefore, these structures can be used as viable conducting wires for flexible electronics.

## RESULTS AND DISCUSSION

The proposed approach to the silver ink adhesion enhancement is illustrated in Figure 1. It consists of four major steps: (i)



**Figure 2.** Scheme of self-assembled layer (SAL) formation during modification of the plasma-treated polymer substrate surface, containing hydroxyl groups, with (3-mercaptopropyl)trimethoxysilane.

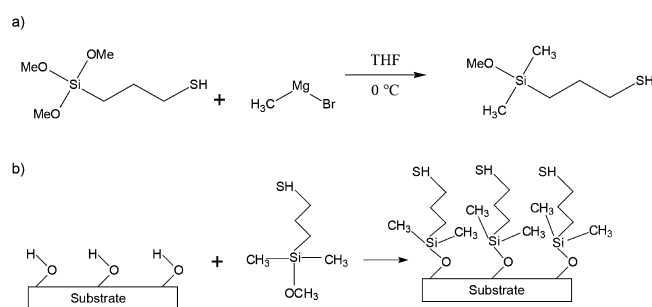
plasma treatment of a polymer substrate, (ii) silanization of the treated polymer surface leading to SALs formation, (iii) silver ink screen-printing, and (iv) curing of the printed ink structures.

**Polymer Surface Modification.** For the first stage, PDMS and PEN substrates were treated by dc discharge plasma at specially selected conditions for each polymer that allow the formation of hydroxyl groups on the substrate surface. Next, the silanization process was carried out using vapor deposition of APTS or MPTS under normal conditions. This silanization process using trimethoxysilanes includes two simultaneous chemical reactions: While a number of the methoxysilane groups react with hydroxyl groups on the substrate surface to form a monolayer, other methoxysilane groups react with each other (reaction scheme in Figure 2), leading to a 3D polymerization and multilayer formation of cross-linked polyorganosiloxanes on the substrate. Additionally, in the case of MPTS, the presence of ambient oxygen is sufficient to oxidize thiols into disulfides,<sup>31</sup> leading to the partial coupling of  $-SH$  groups and the formation of a denser multilayer. AFM data proved multilayer formation with thicknesses of about 10 nm for both PEN and PDMS substrates and both adhesion promoters (SAL and SAM Characterization section).

The silanization of the surface of PDMS by various functional alkoxy silanes has been described for biological applications, such as microfluidic assays<sup>32</sup> or cell adhesion.<sup>33</sup> However, in all of these cases, the modification was made using solutions in organic solvents that could lead to a partial swelling of the PDMS; though not necessarily important for biological applications, this will be a crucial issue in microelectronics applications where the manufactured component must conform to precise dimensions. Recently, it was shown that silver nanoparticles can be firmly grafted on MPTS-functionalized glass surfaces<sup>34</sup> obtained by a similar solution-processed technique. In this work, vapor deposition was chosen as a method of the surface modification in order to prevent swelling of the polymer substrates.

Because the variable thickness of the alkoxy silane SAL could be a disadvantage in a manufacturing process, it was investigated whether a monolayer of the same functionality could enhance the adhesion. (3-Mercaptopropyl)dimethyl(methoxy)silane (mono-SH) was synthesized using a process similar to a method described in the literature<sup>35</sup> with one modification. This was the substitution of methylmagnesium chloride with methylmagnesium bromide, which helped to increase the product yield from 54 to 78% (Figure 3a). The product was used for the silanization under the same conditions

as described above (Figure 3b), leading to monolayer formation.



**Figure 3.** Scheme of (3-mercaptopropyl)dimethyl(methoxy)silane (mono-SH) synthesis (a) and corresponding monolayer formation (b).

To estimate the influence of completion of surface modification by MPTS and APTS on the adhesion properties, the exposure time was varied between 2 and 72 h for both PDMS and PEN substrates. Because the monomethoxy derivative (mono-SH) is not as active as the trimethoxy derivative (MPTS), the layer deposition for mono-SH was carried out for 72 h to ensure that all methoxy groups have reacted with the substrate surface.

**SAL and SAM Characterization.** The modified surfaces of PDMS and PEN substrates were fully characterized by water contact angle (WCA) measurements, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). The WCA data of bare, plasma-treated, and SAL-modified substrates are summarized in Table 1. It can be seen that bare substrates have different wetting ability: PDMS is highly hydrophobic (WCA = 118°), whereas PEN is relatively hydrophilic (WCA = 54°). After the plasma treatment, both substrates become super hydrophilic: WCA decreases up to zero and then increases after modification by SALs. Finally, wetting ability of PDMS slightly improves for all investigated organoalkoxy silanes with the modification time increasing, whereas wetting ability of PEN decreases under the same conditions. These findings can be easily understood, taking into account that the SALs contain the hydrophobic siloxane and alkane groups as well as the hydrophilic thiol or amino groups. Because of the presence of the former, SAL is less hydrophilic than bare PEN substrate, whereas the presence of the latter makes it more hydrophilic than bare PDMS substrate.

**Table 1.** WCA of Bare, Plasma-Treated, and SAL-Modified Substrates

modification method	substrate			
	PDMS		PEN	
	modification time (h)	WCA (deg)	modification time (h)	WCA (deg)
bare		118 ± 5		54 ± 3
plasma-treated		0		0
APTS (–NH <sub>2</sub> )	2	116 ± 3	2	63 ± 3
	15	110 ± 3	15	63 ± 3
	72	110 ± 3	72	63 ± 3
MPTS (–SH)	2	107 ± 3	2	66 ± 3
	15	104 ± 3	15	69 ± 3
	72	99 ± 3	72	79 ± 3
mono-SH	72	110 ± 3	72	63 ± 3

To gain further insight into the surface changes after SAL formation, measurements of the surface free energy (SFE) were carried out (Figure S1, Supporting Information). However, no clear correlation between the SFE and the wettability and further printability of the ink was found. A consistent trend that can be seen in these data is an increasing of the polar component of SFE for SAL-modified substrates compared to those of bare PEN and PDMS. The largest increase of the polar component of SFE was observed for PEN modified with a monomethoxy derivative (mono-SH), which can be explained by the monolayer forming a well-ordered structure with a high surface density of the functional groups. Adhesion is only dependent on the SFE in the case of noncovalent interactions between the layers. In the case of SAL-modified polymers, adhesion improvement was achieved by covalent bonding of silver with the functional mercapto groups or by the formation of coordination bonds between silver and the functional amino groups.

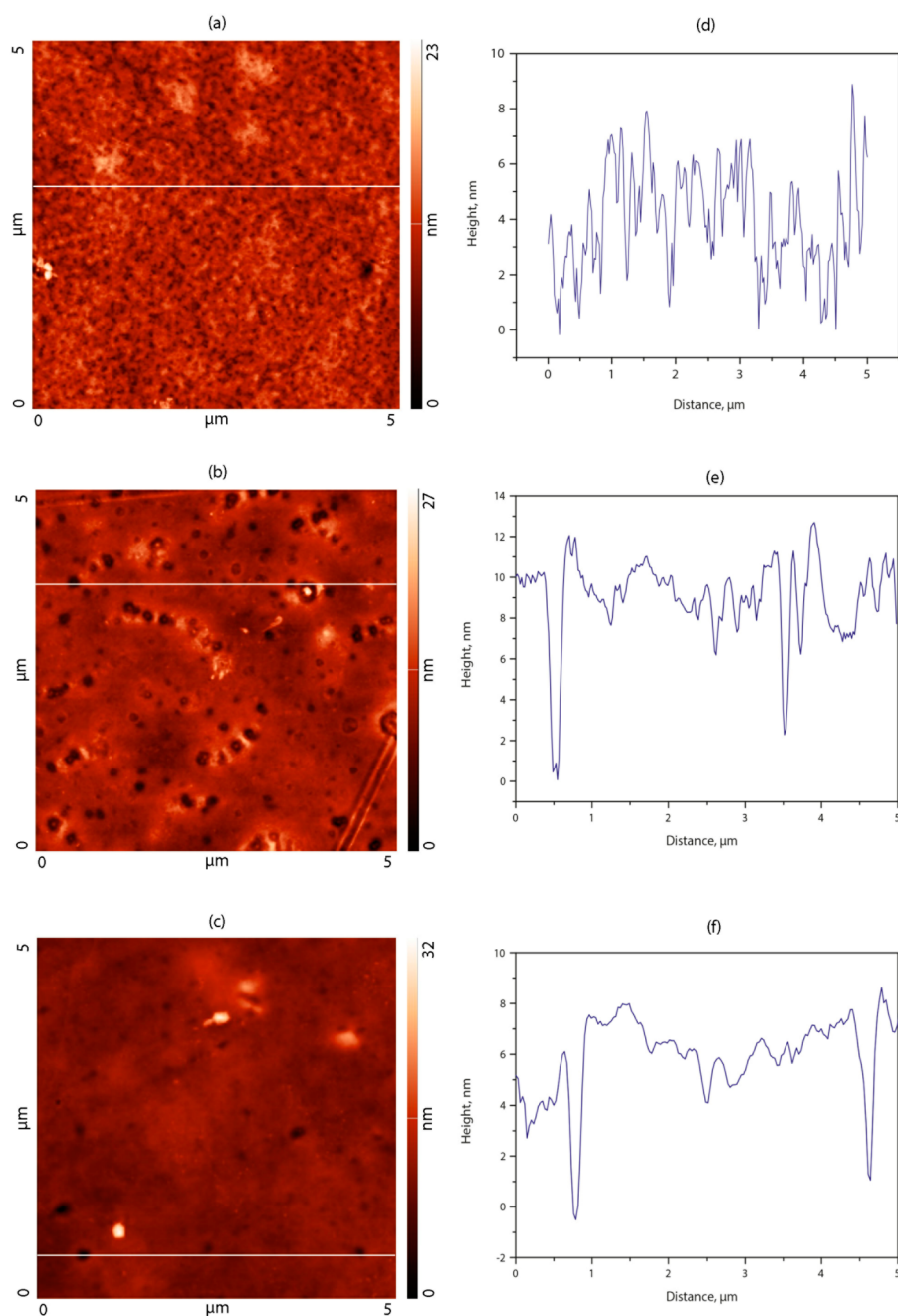
The morphology of bare PEN and PEN modified with MPTS or APTS was studied with AFM (Figure 4). The surface of bare PEN (Figure 4a) demonstrates low RMS roughness of around 1 nm. The film is very homogeneous, which was proven by taking a series of AFM pictures at different parts of the sample. The MPTS-treated samples demonstrate completely different morphology: A homogeneous film covers the whole polymer surface and has a number of holes, confirming SAL formation. The MPTS SAL thickness was estimated to be at least 10 nm, which was the maximum hole depth found on the AFM images. The APTS-treated sample had a similar morphology. However, the observed number of defects, such as holes, was much lower. The thickness of APTS SAL was found to be at least 8 nm. Taking into account that the length of one APTS or MPTS molecule is ca. 0.5 nm, a thickness of 8–10 nm corresponds to multilayer formation for all investigated samples, except mono-SH-modified samples. In the last case, no visible changes of the bare substrate morphology were found because of a small SAM thickness that is comparable with the substrate roughness.

Figure 5a,b shows PDMS surface before and after MPTS treatment, respectively. The morphology changes are similar to those found for MPTS- and APTS-treated PEN substrates discussed above. After silanization, the polymer surface is completely covered with the SAL. The height difference on AFM image of bare PDMS substrate was found to be 1.2 μm. After the treatment, it significantly decreased to 180 nm, which can be explained by the SAL formation followed by the pore

filling with MPTS molecules. The surface smoothness, being a side effect of the silanization process, can potentially improve PDMS properties as a substrate for flexible electronics. Because of a high roughness, the thickness of the modification layer cannot be estimated with AFM. The maximum hole depth was found to be about 80 nm, which is approximately 10 times deeper than the holes found on the modified PEN substrate. Such a big difference is most likely explained by the variation in the initial roughness of the substrates rather than by the difference in the SAL thickness.

To confirm SAL formation on the polymer surface, further characterization of the substrates before and after silanization was made by means of XPS. High-resolution XPS spectra of the N 1s region of PEN modified with SALs of APTS and the S 2p region of PEN and PDMS modified with SALs of MPTS, compared with those of bare PEN and PDMS, are shown in Figure 6. The elemental composition at the surface determined from survey spectra indicates a successful substrate modification with the corresponding alkoxy silane. As expected, there are no nitrogen or sulfur signals in the XPS analysis of bare PEN and PDMS substrates (Figure 6a–c), whereas after their modification by APTS or MPTS N 1s and S 2p peaks are clearly seen on the spectra. N 1s spectrum of APTS-modified PEN (Figure 6a) reveals two-component peak with maximum intensity at a binding energy about 400 eV, which can be associated with a covalent C–N (sp<sup>2</sup>) bond, and a smaller shoulder at a higher energy (401.7 eV), presumably attributed to an ionic bond C–N<sup>+</sup>. S 2p peaks deconvolution (Figure 6b), shown on the spectra as dotted lines, demonstrates that sulfur atoms on MPTS-modified PEN are presented in two different chemical states, which appear as spin–orbit doublets and correspond to two peak positions at 163.6 and 168.1 eV, respectively, and atomic bonds C–SH and C–S–S, respectively. This is evidence that a number of the sulfur atoms in the sample exist in the form of disulfide bonds that can be explained by partial cross-linking between –SH radicals.<sup>36</sup> However, in the case of MPTS-modified PDMS (Figure 6c), such disulfide bonds were not observed; the only doublet peak can be attributed to a thiol C–SH bond.

**Printed Conductive Structures.** To demonstrate the versatility of the SAL-functionalization approach, which could be potentially applied to a broad range of printable materials and polymer substrates, we studied the printability and mechanical properties of two different classes of silver inks, aqueous- and organic-based, on PEN and PDMS substrates. The conductive structures were formed on the treated polymer substrates by means of screen printing, which generally supports reproducible fabrication of the patterns with a spacing of approximately 100–200 μm between the lines. The printing was followed by thermal curing at temperatures as low as 100–150 °C in an oven and gave a silver layer having a thickness of 1–2 μm for aqueous-based PSI-211 ink and 10–15 μm for organic-based CRSN 2442 ink. In contrast to other commonly used printing techniques, screen printing can be achieved with viscous pastes with the silver content reaching as high as 80–90% in some cases. These silver pastes allow the observation of nearly pure interactions between the silver particles and functional groups of the SALs with minimum influence by the solvent. Figure 1 illustrates a proposed mechanism for the bonding of a silver ink to a substrate. Once the ink is printed, the viscosity and wetting behavior dictate the uniformity of the layer, edge definition, and pattern fidelity. A summation of these properties, along with the others, ultimately defines the

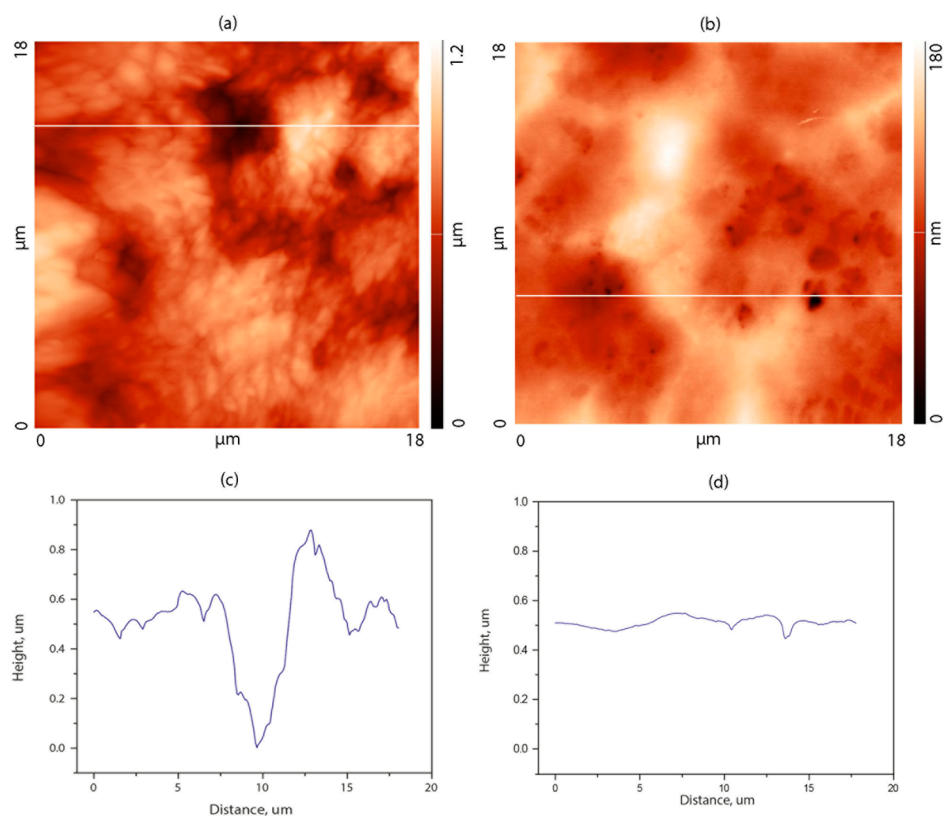


**Figure 4.** AFM height images (a–c) and corresponding cross sections (d–e) for bare PEN (a), PEN modified with self-assembled layer of MPTS (b), and APTS (c). The layer thickness was found to be 10 nm for MPTS (e) and 8 nm for APTS (f).

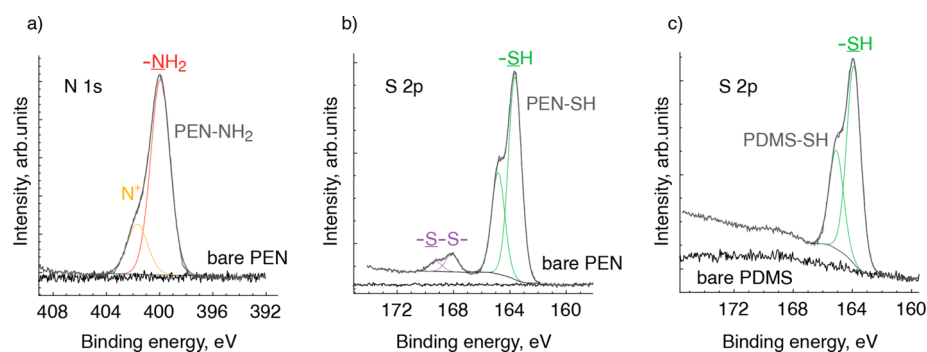
printability of inks. Although the viscosity and the surface tension of the ink are determined by the ink formula, which is defined and optimized by the ink's manufacturer, wettability can be efficiently tuned by modulating the chemical nature of the substrate. Hence, the introduction of functional groups with strong affinity to silver, such as  $-\text{NH}_2$  or  $-\text{SH}$ , onto the surface of naturally inert polymers should lead to better wetting and thus improved printability of the ink. Indeed, as experimentally shown, the SAL modification facilitated a reliable printing of aqueous- and organic-based silver inks on the functionalized PDMS as well as PEN substrates (Figure 7). It should be noted that the conducting layer could not be printed on bare PDMS because of dewetting of the inks (Figure S2, Supporting Information). In the case of PEN, the inks' printability is

satisfactory even on bare PEN, and the images of the conducting layer were approximately the same for bare and modified PEN (Figure 7c,d). The morphology of the silver inks after curing was the same on bare and SAL-modified PEN substrates. For instance, organic silver ink CRSN2442 roughness is about  $0.8 \pm 0.2 \mu\text{m}$ , according to the AFM images (Figure S3, Supporting Information).

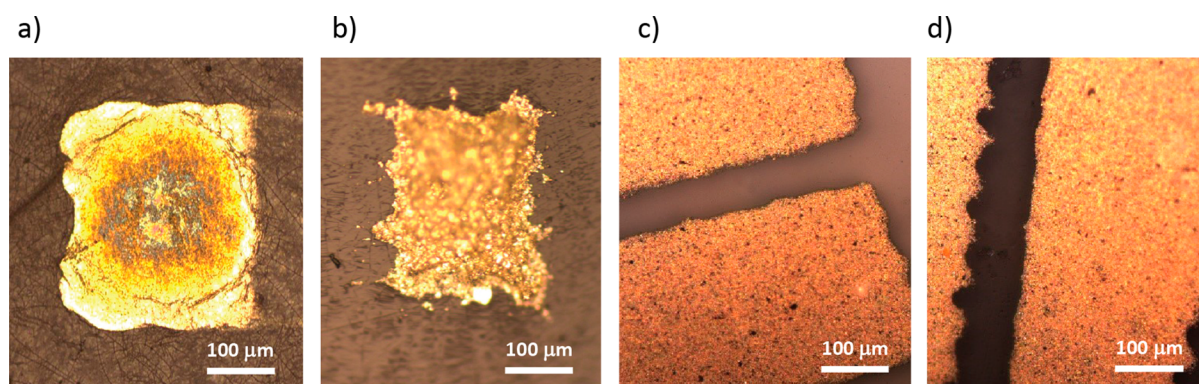
The mechanical properties of printed conductors, including adhesion between the pattern and the substrate, have a significant effect on the optimal performance and reliability of the printed circuit. The adhesion of two materials is governed by the morphological and chemical properties of their interface. Because we typically deal with substrates that lack surface features, the main contribution to adhesion comes from the



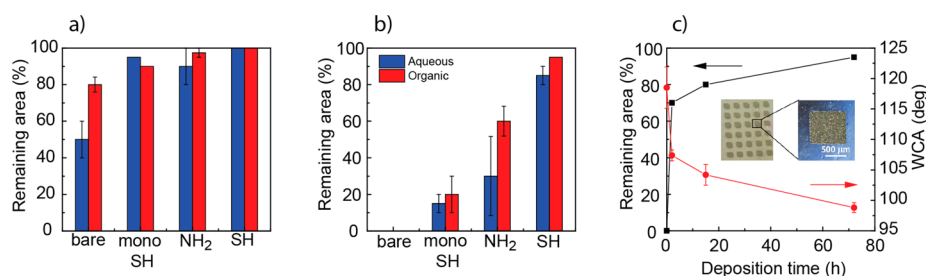
**Figure 5.** AFM height images (a and b) and corresponding cross sections (c and d) for bare PDMS (a and c) and PDMS treated with MPTS (b and d).



**Figure 6.** High-resolution XPS spectra of the N 1s region of bare PEN compared to that of PEN modified with self-assembled layer (SAL) of APTS (a), the S 2p region of bare PEN and PEN modified with SAL of MPTS (b), and the S 2p region of bare PDMS and PDMS modified with SAL of MPTS (c).



**Figure 7.** Optical images of silver structures printed using aqueous PSI-211(a) and organic CRSN2442 (b) inks on MPTS-functionalized PDMS; organic CRSN 2442 ink on bare PEN (c) and SAL-modified PEN (d).



**Figure 8.** Adhesion evaluation results for silver inks PSI-211 (blue) and CRSN2442 (red) printed on SAL-functionalized PEN (a) and PDMS (b) compared to those on bare substrates. The SAL deposition time was 72 h for all samples. (c) Evolution of silver adhesion and water contact angle on SAL-functionalized PDMS with MPTS deposition time. Inset shows the optical images of printed silver structures used for adhesion evaluation tests. The standard error was obtained by measuring three samples.

chemical interactions between the layers. Thus, adding the SAL, which acts as an adhesion promoter, can lead to improved adhesion by altering the chemical nature of the polymer surface that strongly bonds to the silver layer. After printing the inks, the resulting structure is composed of silver particles stabilized by surfactants (or other organic stabilizers, Figure 1) preventing particle agglomeration and sedimentation in the liquid ink. Because of the presence of this layer of organic molecules surrounding the particles, their interactions with the neighboring particles and the surface of the substrate are limited; however, the reactive  $-SH$  or  $-NH_2$  located at the top of the SAL may partially substitute for the stabilizer and bind with the silver. Regardless of these potential interactions, it is proposed that the bonding of silver to the polymer surface via SAL occurs mainly during the sintering step when the sample is heated. The curing process involves a melting and merging of the particles concomitant with the degradation of the organic stabilizer and evaporation of the solvent. During the sintering process, the SALs described above can sustain such temperatures without destruction because they are covalently bonded to the substrate and have an organosilicon nature, which is highly thermostable.

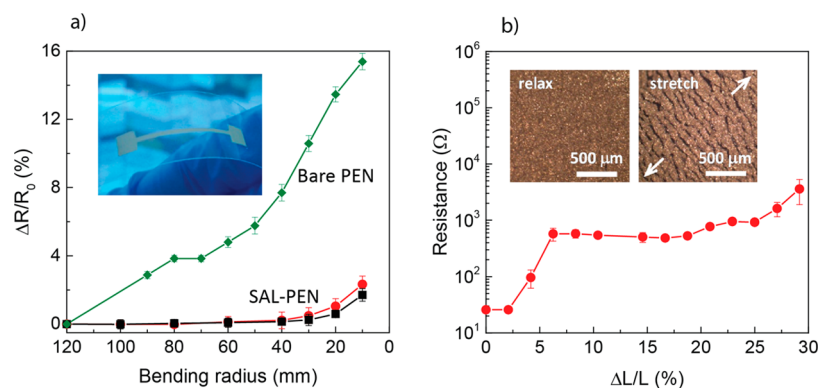
A conventional tape test, described in the Experimental section, was utilized to measure the adhesive strength between the cured ink and the polymer substrate. As shown in Figure 8, the SALs strongly contribute to the adhesion of silver on both PEN and PDMS substrates. The  $-SH$  groups showed higher impact on the final adhesive strength than  $-NH_2$ , which is in good agreement with the fact that silver has a higher affinity to thiol than to amino groups. In other words,  $-SH$  works better than  $-NH_2$  in terms of adhesion improvement because thiol–silver interactions have a covalent nature that leads to the formation of strong  $Ag-S$  bonds, whereas complex formation between silver and amine species typically results in less energetic noncovalent forces. It has been reported that binding a silver ink to PEN is relatively easily achievable by specific ink formulation,<sup>11</sup> whereas the enhancement of silver adhesion to PDMS has been rarely reported because of the challenge of activating a surface that has an extremely low SFE of about 20 mN/m.<sup>37</sup> This work shows that the adhesion of silver to a SAL-modified PDMS substrate can achieve 85–95% of the remaining area after a tape test (Figure 8b) compared to 0% of the bare PDMS substrate, and it is believed that further improvement up to 100% is possible. Comparing layers to monolayers formed by thiol-containing SAMs, it appeared that SAMs are less efficient than the SALs in terms of adhesion promotion (Figure 8a,b), probably because of incomplete coverage of the surface, as has been reported in the literature

(see below). Moreover, it should be noted that once the SAL is deposited, the substrate can last for at least 6 months without losing its active surface property (data not shown).

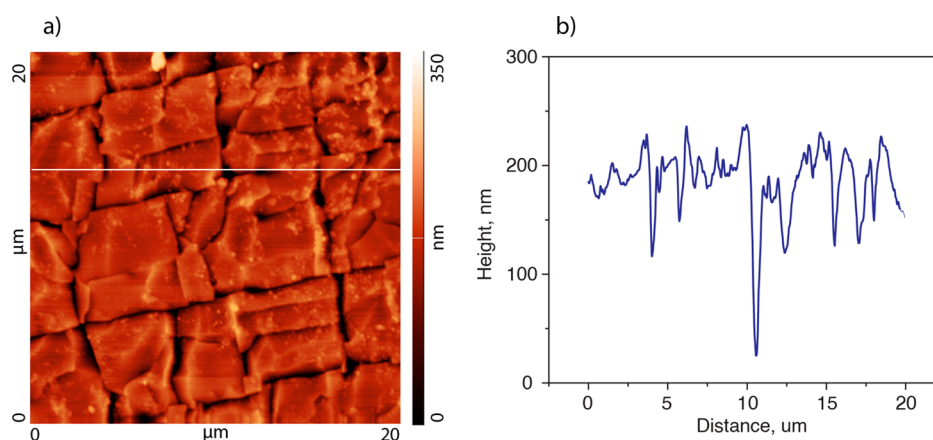
The processes associated with self-assembly of alkoxy-silanes on a surface are usually slow. Nevertheless, a remarkable degree of adhesion of silver on PDMS can be achieved within 2 h of MPTS deposition (Figure 8c). This slowly approaches nearly 100% during the next 70 h. This can be explained by a limited reaction rate of the SAL formation on the polymer surface, which builds up as separate islands, giving a continuous layer over the course of time.<sup>38</sup> As can be seen from the data obtained (Table 1 and Figure 8), an enhancement of adhesion on PDMS is accompanied by a decrease of WCA, indicating an increase in the SFE, high values of which are typically a prerequisite for strong molecular forces at the interface. Regarding the PEN substrate, less than 15 h of vapor deposition is normally required to achieve nearly perfect adhesion of the silver inks.

Conductive inks containing highly concentrated metal particles are key materials in the fabrication of printed conductors on flexible substrates, which ideally should be able to maintain their electrical properties even during mechanical deformations. In this work, we demonstrate that the silver patterns printed on SAL-functionalized substrates possess a relatively low electrical resistance in the range of 0.10–0.14  $\Omega/sq$  for PEN and 0.15–0.73  $\Omega/sq$  for PDMS. The thickness measured by white-light interferometry was about 1–2  $\mu m$  for aqueous-based PSI-211 ink and 10–15  $\mu m$  for organic-based CRSN2442 ink. The resistance appeared to be slightly higher than that of the silver ink printed on the bare PEN substrate ( $0.10 \pm 0.02 \Omega/sq$  for PSI-211 and  $0.05 \pm 0.02 \Omega/sq$  for CRSN2442). This can be explained by the possible diffusion of the remaining unbound APTS or MPTS molecules from the surface into the wet ink, which could later prevent formation of the interparticle contacts during sintering. Taking this into account, the conductivity of printed ink can be further improved by optimizing the SAL deposition process. Note that the resistance of PSI-211 on PDMS was hardly measurable because of the small thickness of the silver layer and the high roughness of the PDMS surface, so it required more than three additional printing runs to achieve sufficient electrical conductance on the SAM-modified PDMS. Conductivity of PSI-211 silver layers on bare PDMS was not evaluated since the wettability was so poor that it was even not possible to form a continuous track.

The use of printed silver conductors in system-on-foil technologies requires the ability to conform to curved surfaces and accommodate mechanical deformations. Therefore, it is



**Figure 9.** (a) Relative resistance changes with bending for CRSN2442 on bare PEN (green curve), and PSI-211 and CRSN2442 on SAL-PEN (black and red curves, respectively); the standard error was obtained by measuring four devices. (b) Resistance–strain relationship of printed CRSN2442 ink on SAL-PDMS at the stretching rate of 10 mm/min; inset presents optical images of silver layer before and after stretching.



**Figure 10.** (a) AFM image and (b) corresponding cross-sectional representation of PDMS substrate modified by MPTS with printed PSI-211 ink after stretching.

useful to investigate the mechanical properties, in particular a sustainability of electrical properties under different strains. In the case of flexible but inextensible PEN substrates, the study of bending behavior of the structure under relatively low strains is of main interest, but as for readily stretchable PDMS substrates, it is more interesting to observe conductivity changes upon stretching under high strain values because it is difficult to separate the bending and stretching effect for silicone resins. The printed structures made of PSI-211 and CRSN2442 inks on SAL-functionalized PEN can reversibly bend at least up to 20 mm of bending radius, which corresponds to approximately 0.3% of tensile strain calculated according to the bending strain theory, with less than 1% of relative resistance change (Figure 9a, red and black lines). Comparing these data with the corresponding data obtained for CRSN2442 inks on bare PEN (Figure 9a, green line) it is clearly seen that modification of the PEN substrate by SAL leads to the significant decrease of relative resistance change (from 14 to 1% at 20 mm of bending radius). Note that such deviations can be significantly reduced by applying a silver ink that has enhanced mechanical properties. The silver structures printed with CRSN2442 ink on SAL-modified PDMS were elongated to a larger strain of 30% without losing the ability to conduct current (Figure 9b). However, stretching the polymer generated a large number of cracks in the film, which led to a significant increase in resistance (Figure 10). Nevertheless, the silver exhibited excellent adhesion and sustained multiple stretching cycles

without apparent delamination, demonstrating that conductive structures on SAL-functionalized PDMS can be used in circuits that encounter moderate mechanical stress.

## CONCLUSIONS

An approach to a polymer surface modification by SALs of functional alkoxy silanes has been developed that allows enhanced adhesion between a metal conducting layer and a flexible polymer substrate. The approach supports 100% adhesion for water- and organic-based silver inks on PEN and PDMS substrates. The printed conducting structures on SAL-functionalized PEN exhibit the relatively low sheet resistance up to 0.1  $\Omega$ /sq and can be reversibly bent at least up to 20 mm of bending radius with less than 1% of relative resistance change. The silver layer on SAL-functionalized PDMS exhibits excellent adhesion and sustains multiple stretching cycles without apparent delamination. The reported approach seems to be universally applicable and potentially could be extended to other metal inks such as gold, copper, nickel, etc., paving the way to efficient printing of highly conductive structures on flexible and stretchable substrates.

## EXPERIMENTAL SECTION

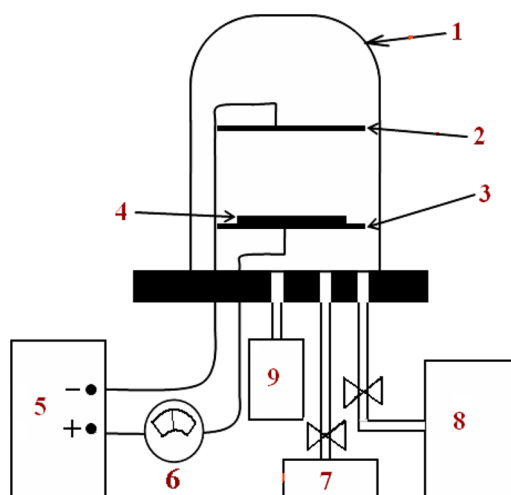
**Materials.** Toluene (Acros) was distilled over sodium before use. Isopropanol (Acros) was used as received. Ultrapure water obtained from an Akvilon deionizer D-301 system was used for the substrate cleaning. PEN substrate was 125  $\mu$ m thick poly(ethylene naphthalate)



foil (Teonex Q65FA, DuPont Teijin Films). PDMS substrate was a homemade 1 mm thick PDMS layer obtained from commercially available Dow Corning Sylgard 184 silicon elastomer kit, used as described by the manufacturer. (3-Mercaptopropyl)trimethoxysilane (MPTS) was received from Aldrich, and (3-aminopropyl)trimethoxysilane (APTS) was received from Acros Organics. Both MPTS and APTS were used as received. The silver aqueous ink PSI-211 was supplied by PChem, and silver organic-based ink was CRSN2442 supplied by Sun Chemical and used as described by the manufacturer.

**(3-Mercaptopropyl)dimethyl(methoxy)silane.** A 3 M solution of  $\text{CH}_3\text{MgBr}$  in diethyl ether (50 mL, 0.15 mol) was added dropwise to a solution of 3-mercaptopropyltrimethoxysilane (8.5 g, 0.043 mol) in 50 mL of THF, while the temperature was kept between 0 and +10 °C. The reaction mixture was stirred for 1 h at 0 °C and then treated dropwise with  $\text{CH}_3\text{OH}$  (40 mL). The solid was filtered. The product was purified by distillation in vacuum (80 mbar, 107–109 °C; lit.: 60 Torr, 90–110 °C)<sup>35</sup> to give pure (5.51 g, 78%) product as a colorless liquid.  $^1\text{H}$  NMR ( $\delta$  in  $\text{CDCl}_3$ , TMS/ppm): 0.10 (s, 6H,  $\text{SiCH}_3$ ), 0.69 (m, 2H,  $\text{SiCH}_2$ ), 1.34 (t, 1H,  $J = 7.9$  Hz, SH), 1.65 (m, 2H,  $\text{SiCH}_2\text{CH}_2$ ), 2.53 (q, 2H,  $J = 7.3$  Hz,  $\text{Si}(\text{CH}_2)\text{CH}_2$ ), 3.42 (s, 3H,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR ( $\delta$  in  $\text{CDCl}_3$ ) -2.73, 15.09, 27.93, 28.05, 50.22.  $^{29}\text{Si}$  NMR ( $\delta$  in  $\text{CDCl}_3$ ) 18.98.

**Plasma Modification.** Plasma modification of the polymer films was carried out using a dc discharge and vacuum setup (Figure 11).



**Figure 11.** Scheme of a dc discharge setup: (1) vacuum reaction chamber, (2) cathode, (3) anode, (4) film sample, (5) dc power supply, (6) current meter, (7) gas inlet, (8) vacuum pump, and (9) pressure gauge.

The polymer samples were placed inside a vacuum reaction chamber (1) on an aluminum anode (3) (18 cm in diameter; 5 cm distance between the electrodes) and treated by dc discharge induced from the dc power supply (5). In the case of PEN modification, the reaction chamber was preliminarily evacuated to  $\sim 10$  Pa; then, the samples were treated at air pressure of 10 Pa and a discharge current of 50 mA for 60 s. Under evacuation of the reaction chamber, PDMS films were characterized by the substantially higher outgassing rate than PEN films. In this case, the reaction chamber was preliminary evacuated to  $\sim 4$  Pa, then filled with air to a pressure of  $\sim 500$  Pa, and then evacuated to a pressure of  $\sim 10$  Pa. After reaching of this pressure, the polymer sample was treated at a discharge current of 50 mA for 60 s. Filtered air was used as a working gas. All samples were put in deionized water immediately after the plasma treatment was complete in order to remove electrical charge from the film surface.

**Chemical Surface Modification.** Chemical surface modification of the substrates was carried out immediately after the plasma modification using vapor deposition of alkoxy silane (3-aminopropyltrimethoxysilane or 3-mercaptopropyltrimethoxysilane). Polymer films

were dried from water using precision wipes (KimtechScience from Kimberly-Clark) and put into Petri dishes. Alkoxy silane (2–3 drops) was added to every dish, and then the dishes were closed and left at room temperature for 2–72 h. The droplets were about 50  $\mu\text{L}$ ; they were deposited next to the polymer films inside glass Petri dishes that did not require being sealed. The time of the droplet evaporation was larger than the modification time in all cases. Modified substrates were used in subsequent experiments without any additional treatments.

**Thin Film Characterization.** AFM studies were performed with NT-MDT Solver NEXT instrument in semicontact mode used in an ambient environment. Commercially available standard silicon probes Brücker FESPA with resonance frequency of 70 kHz were used. XPS measurements were performed on a Kratos Axis Ultra DLD setup with a monochromatic  $\text{Al K}\alpha$  X-ray source (1486.6 eV) at pass energy 160 eV for survey spectra and 23.5 eV for narrow element peaks. The chemical states of the elements were interpreted using ref 32 and ref 36.

**Printing Technique.** Structures for adhesion tests were fabricated using screen printing. The manual screen printing table, made according to a special order by Europrint, Ltd. (Saint Petersburg, Russia), was used. The inks were deposited using a polyester screen mesh of 120 threads/cm with a thread diameter of 35  $\mu\text{m}$  and a squeegee with the hardness of 75 Shore A. Feature printing was followed by a curing step. The wet ink was sintered in a drying oven at 120 °C for 10 min (PSI-211) and at 150 °C for 30 min (CRSN2442).

**Characterization Techniques.** The printed samples were inspected by optical microscopy using a Carl Zeiss Axiomager. The thickness was measured by means of white-light interferometer (MicroXAM-100 from KLA-Tencor). Contact angles of test liquids (distilled water, tetradecane, and glycerol) were recorded using Kruss EasyDrop drop shape analyzer. Five droplets, 2  $\mu\text{L}$  in volume, were measured on bare and SAL-modified polymer surfaces; then, contact angles and SFEs were estimated using the method after Wu in the software program provided by the manufacturer. For each sample, standard deviation was calculated. The adhesion was evaluated by scratch tests and cross-cut tape tests based on the standard ASTM D 3359. The sheet resistance values were calculated on the basis of standard 4-point probe measurements using the Agilent 34410A digital multimeter. Mechanical properties of the printed tracks were studied by applying a tensile bending stress with the radius of curvature ranging from 120 to 10 mm. Mechanical properties of stretchable substrates were studied using a Mecmesin MultiTest system.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Plots of surface free-energy values for bare and SAL-modified PEN and PDMS, microphotograph of the silver structure printed using aqueous PSI-211 ink on bare PDMS, and AFM image of the organic silver ink SRCN2442 printed on PEN substrate. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/am508905t.

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### Notes

The authors declare no competing financial interest.

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