We describe a new facile chemistry-based technique for patterning films of organic conductors on a polymeric substrate that consists of directly writing on the organic conducting surface using a local heat source such as a laser beam.

Developing facile routes for patterning organic materials compatible with their processing stages is crucial in order to integrate the high performances reported in organic devices, such as organic field-effect transistors (OFETs), light-emitting diodes (LEDs) and solar cells, into circuits. The most attractively viewed patterning techniques for low-cost technology entail printing methods, and they are being widely explored for the fabrication of devices. However, all such techniques typically require multiple stages and transfer of materials between substrates. Additionally, it is often necessary to employ solvents which can deteriorate the organic materials. Hence, for the immense potential of new organic devices to be realized in integrated circuits, it is imperative to find alternative direct patterning methods. Here we report on an exceptionally facile one-step direct-writing technique for patterning organic conducting films which benefit from the chemistry of the organic molecular conductors. We further demonstrate the potential of this novel technique for the design of electronic components and devices.

Novel composite materials called bi-layer (BL) films, which consist of a polymeric matrix with a top layer formed by a nanocrystalline or microcrystalline network of a tetrathiafulvalene (TTF) based conductor, were previously reported. Additionally, these molecular conductors can be converted by the action of temperature or an electron beam from a semiconducting phase to a metal-like one, and/or degrade it to a non-conducting derivative.

Two types of BL films were prepared as previously reported. The first film was based on a polycarbonate matrix containing a semiconductor top layer of crystals of \( \alpha \)-BEDT-TTF\( _2 \)I\( _3 \) (BL film 1) [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene], and the second one on a polycarbonate matrix with a top metallic crystalline layer of \( \beta \)-BET-TTF\( _2 \)I\( _3 \) (BL film 2) [BET-TTF = bis(ethylendithio)tetrathiafulvalene]. The surface of the polycarbonate films, with a typical thickness of 20 \( \mu \)m and containing 2 wt% of the molecularly dispersed TTF derivative, were treated with vapors of an I\( _2 \)-CH\( _2 \)Cl\( _2 \) solution. This process resulted in the film swelling and a surface chemical reaction that led to the formation of a conducting network of micro- and nanocrystals of the corresponding TTF salt on the film surface. The X-ray diffraction patterns of the BL films 1 and 2 show only the presence of (00\( l \)) reflections indicating that the crystals of the TTF salts are oriented, the \( c^* \)-axis being perpendicular to the film surface (see ESI†). The measured values of the \( d_{00l} \) interplanar spacings along with the (00\( l \)) reflections intensities confirmed the identity of the phases of the known TTF based organic conductors.

The room temperature conductivities of BL films 1 and 2 were found to be 5–10 \( \Omega^{-1} \) cm\(^{-1} \).

Fig. 1 (left) shows a scanning electronic microscope (SEM) image of the cross-section of the BL film 2. In this image the conducting and insulating layers of the film are clearly differentiated. The Energy Dispersion X-ray spectroscopy (EDX) analysis of the sulfur and iodine contents (Fig. 1, right) proved, for the first time, that the conducting layer in the film is mainly formed in the first 1–1.5 \( \mu \)m of depth.

BL films offer promising prospects for applications where large area coverage of organic conductors and flexible substrates are required. The films are stable for years without showing any change in their conductivity. They can be produced easily and at low cost without the need for using large quantities of the organic precursor compound. Nevertheless, the design of electronic components or devices calls for patterning techniques that permit one to place the organic conductors on the substrate at will. We report here a novel technique, namely thermochemical printing of organic conductors (TCPOC), for patterning the BL films. The patterning was realized employing a local heat source and by taking advantage of the chemistry of the organic conductors, as at high temperature the iodine forming the conducting TTF-based crystals can be partially or totally removed. Consequently, by locally heating the film surface, the conducting areas, formed by...
the TTF salts, can be converted into insulating areas, formed mainly by the neutral TTF derivatives, following the reactions

\[ 2(\text{BEDT-TTF})_2\text{I}_3 \xrightarrow{\Delta} 4\text{BEDT-TTF} + 3\text{I}_2 \]

\[ 2(\text{BET-TTF})_2\text{I}_3 \xrightarrow{\Delta} 5\text{BET-TTF} + 3\text{I}_2 \]

We used as a heat source a 1064 nm Nd:YAG laser with a maximum output of 1 W and focused down to a micron-sized spot to heat locally the sample. Thus, by simply writing directly on the conducting film surface with this laser beam we were able to pattern these BL films.

BL films 1 and 2 were inspected by Scanning Electron Microscopy (SEM) before and after exposure to the laser light. We observed that in both cases the film morphology was modified after irradiation implying that a new material was formed on the film surface (see SEM images in ESI).

The EDX analysis of the BL films revealed that in the laser exposed areas the atomic percentage of iodine strongly diminished, whereas the percentage of sulfur increased. The relative atomic proportions of S and I for BL film 1 changed from 85% and 15% (before laser irradiation) to 98% and 2% (after laser exposure), respectively. Similarly for BL film 2, the relative proportions of S and I were 83% and 17% (before laser irradiation) and 93% and 7% (after laser exposure), respectively. This result is in agreement with the fact that most of the iodine is removed after irradiation due to the heat provided by the laser light source and, therefore, the relative proportion of sulfur increases.

The film resistance in a laser exposed area was found to be larger than 200 MΩ, which corresponds to a conductivity value lower than \(10^{-3} \, \Omega^{-1} \, \text{cm}^{-1}\). This means that the conductivity difference between the irradiated and non-irradiated film regions is of more than six orders of magnitude. In addition, we also studied the local surface electrical properties in the laser exposed and unexposed film areas by conductive atomic force microscopy (cAFM). The acquired current–voltage \((I–V)\) curves corroborated that the laser exposed areas were not conducting; whereas the non-irradiated areas maintained their conductivity properties.

In order to show the versatility and potential of patterning these BL films, we fabricated three possible micro-devices based on the BL film 2. Optical microscope images of the patterned films are shown in Fig. 2 and 3, where the dark areas correspond to conducting zones formed by \(\beta\)-(BET-TTF)\(_2\)\text{I}_3 crystallites and the light areas correspond to the laser drawing paths and are, thus, insulating.

Fig. 2 (right) shows a micro-scale resistor, the resistance value \((R)\) of which depends on the number and length of the fingers (i.e. the total length of the conductive path) as well as the width of each conducting finger.

The pattern in Fig. 3a was performed to use the film as organic interdigitated electrodes or as a planar capacitor, the characteristics of which depend on the number, length, and width of the insulating fingers. Fig. 3b is a fragment of a grid-like pattern to fabricate a multi-cell coplanar capacitor when a second conducting layer is placed on the opposite side of the film and separated from the first grid by an internal polymeric insulating layer.

Overall, the relevance of this novel patterning technique lies in the fact that is a one-step process carried out directly on the conducting surface, thus avoiding the usual transfer steps. Furthermore, once the conducting surface is formed, there is no need to use organic solvents that could damage the organic material. The resolution of the method reported here (approximately 0.8 μm for our setup) is limited to the beam diameter. However, by using as heat sources an electron beam the process could reach nanoscale resolutions. Another strategy could also be the use of masks in order to pattern larger areas simultaneously. Importantly, the challenge of adapting the widely used techniques for micro- and nanofabrication—photolithography, electron beam lithography and related methods—to applications in the field of plastic electronics could be overcome here since no additional resists and solvents would be required. Currently, we are working in this direction.

In conclusion, we described here a new chemistry-based technique for patterning BL films formed of organic conductors on a polymeric substrate. This facile one-step process consists of directly writing on an organic conducting surface using a local heat source such as a laser beam. This process represents a large step forward towards the strongly pursued goal of preparing all-organic electronic components and devices for plastic electronics.

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Notes and references