Supplementary material (ESI) for Journal of Materials Chemistry

SUPPORTING INFORMATION

Direct Micro-Patterning of TTF-Based Organic Conductors on Flexible Substrates

By Marta Mas-Torrent, Elena E. Laukhina,* Vladimir Laukhin, Caitriona M. Creely, Dmitri V. Petrov, Concepció Rovira and Jaume Veciana*

Experimental section

BL films preparation. Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), Poly-(Bisphenol-A-carbonate) (PC) in pellets (average M_w ca. 64,000) and 1,2-dichlorobenzene were purchased from Aldrich and no further purification was carried out. Bis(ethylenethio)tetrathiafulvalene (BET-TTF) was synthesized as previously reported.[1]

PC films (10-20 μm thickness) with molecularly dispersed BEDT-TTF or BET-TTF (2 wt. %) were cast onto a glass surface at 130°C from 1,2-dichlorobenzene (50 ml) containing BEDT-TTF or BET-TTF (0.02 g) and PC (0.98 g). Subsequently, the film surface was treated with vapors from a saturated solution of I_2 in CH_2Cl_2. In a first step, a glass flask containing the binary system of the saturated I_2/CH_2Cl_2 solution and I_2/CH_2Cl_2 vapor in equilibrium was enclosed in the chamber of a thermostat and left to equilibrate at 23°C for 45 min. Subsequently, the samples were treated with vapors of solvent and oxidant by placing them as a lid at the top of the flask.

Patterning. The laser used to pattern the sample was a 1064 nm Nd:Yag laser (Laser Quantum) with max output of 1 W, chosen so as to be absorbed by the film. The laser was collimated and aligned into an inverted microscope (Olympus IX 51) such that the beam was focussed by the objective (20X, 0.4 NA) at a sample holder fixed to a motorised stage. The power at the sample plane was 0.9 mW, yielding a power density of approx 1kW cm^{-2}, using an estimated spot size of 5 microns.

The micron movement of the sample holder relative to the laser beam was achieved by motorised actuator control in 2 axes (Thorlabs, actuator Z625B, DCX-PCI 100 controller). The software used to control the movement was Thorlabs motion control API 'C' sample program v 3.2.1.20. This allowed for control of the velocity of the movement as well as specifying the direction and total length of travel. After experimentation with different velocities the maximum of 360 μm s^{-1} was used, as the patterning effect due to the local heating was practically instantaneous.

It should be noted that a change in the thickness of the film will cause the distance between film surface and microscope objective to change and thus the size of the spot patterned on the film will change. Also in earlier trials we noted that any defects in the film can cause burning, so that a good quality, flat film is essential for this technique.

Sample characterization. X-Ray diffractograms of the films were recorded on a Siemens D-500 diffractometer in the reflection mode with monochromatic Cu-Kα (1,54056 Å). Energy Dispersion X-ray spectroscopy (EDX) analysis was performed by a scanning electron microscope (SEM) HITACHI S-3000N with an EDX-NORAN instrument. The well known $(BEDT\text{-}TTF)_2I_3$ molecular crystals were used as the standard for calibration. Scanning electron microscopy (SEM) images were acquired on a Hitachi S-570 system operating at 20 kV. Temperature resistance dependence of BL films (macroscopic transport properties) were measured using a standard 4-probe dc-method. Rectangular pieces (≅1.5x0.5 mm^2) were cut out from the film samples and, subsequently, four annealed platinum wires (20 μm in diameter) were attached to the conducting surface of the film sample using a conductive graphite paste. The micro-transport properties of the patterns were studied using microscopy techniques. Surface analysis at nanometer scale was performed by Atomic Force Microscopy (AFM) using a commercial scanning force microscope

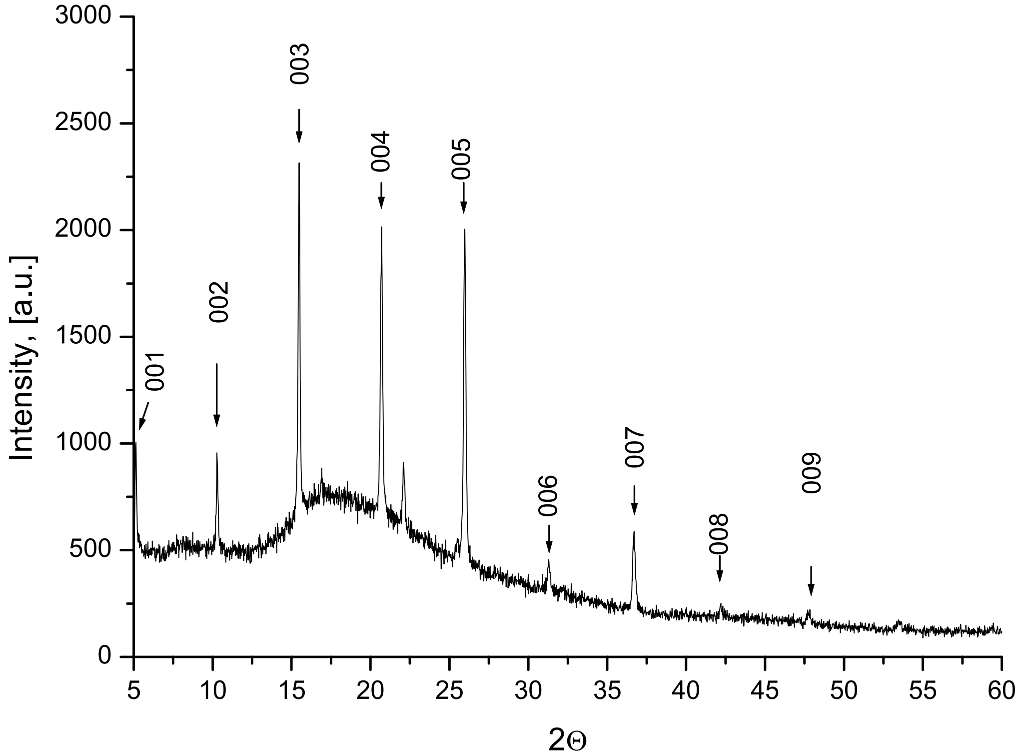
PicoSPM from Molecular Imaging operating in air at room temperature; the I-V responses were acquired scanning locally the dc current through the tip-sample junction while sweeping the applied bias voltage.

Reference

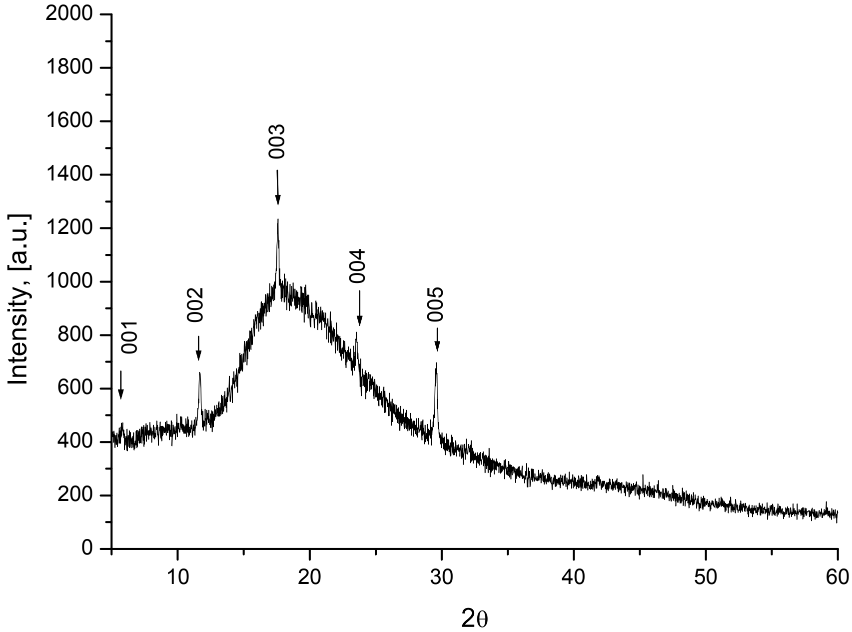
1. A. Pérez-Benítez, J. Tarrés, E. Ribera, J. Veciana and C. Rovira, *Síntesis-Stuttgard*, 1999, **4**, 577.

X- Ray Diffraction Patterns:

1. BL film of α-(BEDT-TTF)$_2$I$_3$



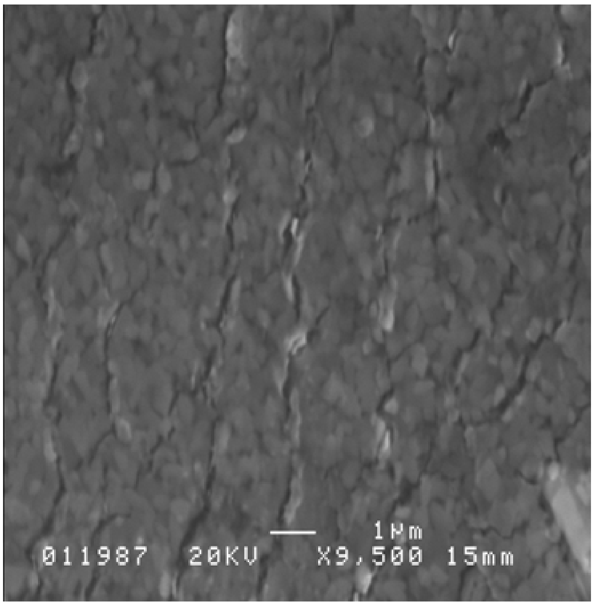
2. BL film of β-$(BET\text{-}TTF)_{2.5}I_3$



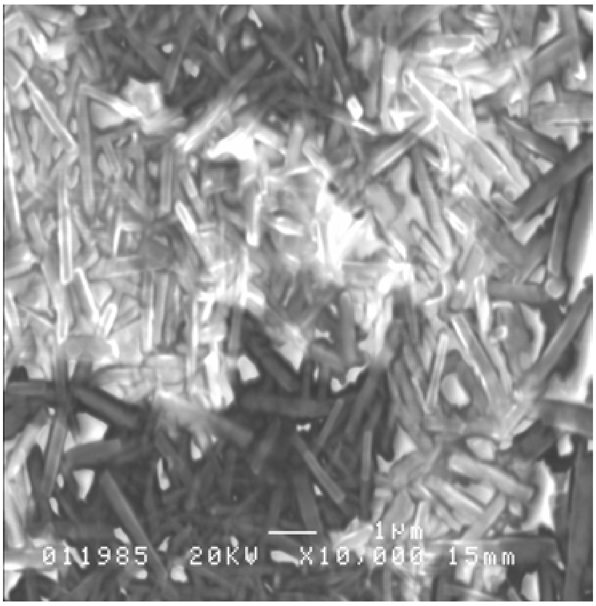
SEM images:

1. BL film of α-$(BEDT\text{-}TTF)_2I_3$

a) Before laser irradiation:

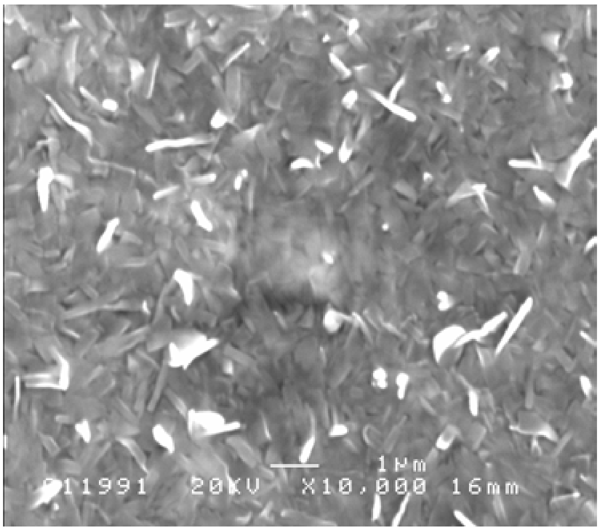


b) After laser irradiation:



2. BL film of β-(BET-TTF)$_{2.5}$I$_3$

a) Before laser irradiation:



b) After laser irradiation: