SUPPORTING INFORMATION

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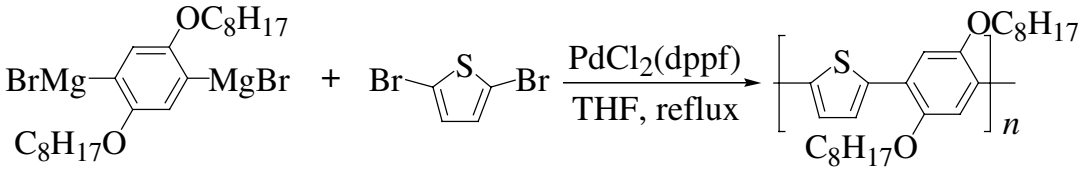
EXPERIMENTAL DETAILS

Synthesis. The synthesis of poly(2,5-dioctyloxy-1,4-phenylene-alt-2,5-thienylene) (POPT) was performed by Pd-catalyzed cross-coupling reaction of bis-organomagnesium reagent deriving from 1,4-dibromo-2,5-dioctyloxybenzene and 2,5-dibromothiophene (scheme 1)

Scheme 1



(POPT)

Molecular masses (M_n = 4260, M_w= 7080, M_w/M_n = 1.67) of the material were determined by Gel Permeation Chromatography (GPC), with uniform polystyrene standards.

Details on the synthesis and characterization of this polymer are reported elsewhere.[1]

Langmuir experiments. Chloroform (Fluka, HPLC grade) was used in making up the spreading solution: 1.91 mg of POPT (4.3×10^{-4} mol, repeat unit) were dissolved in 10 ml of chloroform. Langmuir experiments were carried out using a KSV5000 System3 apparatus. Ultrapure water (resistivity greater than 18 M cm) from a Milli-Q system was used as the subphase (pH 5.9). A 200 l aliquot of the spreading solution was spread onto the subphase. After solvent evaporation, the floating film was compressed at a speed of 5 $Å^2$ $molecule^{-1}$ min^{-1}. During the depositions, the transfer surface pressure was fixed at 19 mN m^{-1}. Glass, quartz and silicon substrates were all rendered

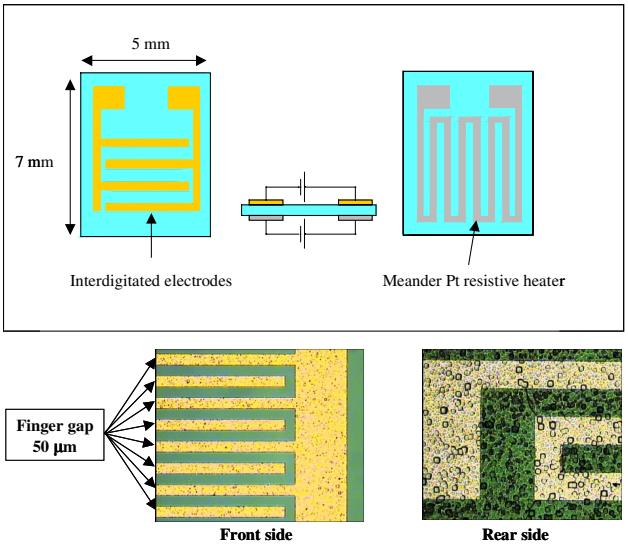
hydrophobic before deposition by storing overnight in a dessicator in contact with vapors of 1,1,1,6,6,6-hexamethydisilazane. The transfer onto all substrates was performed by the horizontal lifting method (Langmuir-Schäfer technique).

Reflection spectroscopy and Brewster Angle Microscopy. Reflection spectroscopy and Brewster Angle Microscopy (BAM) analysis were carried out using a NIMA 601BAM apparatus. Also in this case, a compression speed of 5 $Å^2$ $molecule^{-1}$ min^{-1} was utilized. The reflection data (R) were obtained by an NFT RefSpec instrument. They were acquired under normal incidence of radiation according to the description given in [2] and correspond to the difference between the reflectivities of the floating film/liquid interface and the clean air/liquid interface. Concerning BAM measurements, they were obtained by a NFT BAM2*plus* system with a lateral resolution of 2 m.

Electronic absorption spectra carried out on 30 layers LS thin films were obtained by using a Varian Cary 500 dual beam spectrophotometer in the 300-700 nm spectral range. Samples having the same number of layers were used for optical and electrical characterization.

Device preparation and gas-sensing investigations. Electrical investigations were performed on thin films deposited onto alumina substrates (35 x 10 mm^2, 600 m thick), containing 10 sensors (5 x 7 mm^2). Comb-like electrical contacts were realized onto the front side of each sensor by means of standard photolithographic process. The substrates were coated by a 1.2 m thick film of positive photoresist by using a spinner at 3000 rpm for 30 min. Then, the samples were put into an oven at 90 °C for 30 min to eliminate the solvent from the photoresist layer. The alignment of the masks (made in chromed quartz), the exposition and the development of the photoresist were performed by an alignment instrument, that gives out UV radiation in the wavelength range 350-500 nm and is

characterized by a high alignment accuracy (0.1 m) and high resolution (0.8 m). The metal contacts were deposited by an e-beam evaporator in HV condition (5-8 x 10^{-6} mbar). In particular a 50 nm thick layer of titanium was first deposited and then a 300 nm thick layer of gold. Subsequently the metallic layers were lift-off by treatment in hot acetone, ultrasounds and nitrogen flow to remove the photoresist layer and possible metallic residual that could cause short-circuit. An electrode geometry containing a pair of 24 fingers separated by 50 m was realized. In Figure 1 the final contact geometry is reported. A meander Pt resistive type heater was evaporated on the back side of the alumina substrate by the same photolithographic process. Each sensor was then soldered onto TO-8 support by using gold wires



as suspended devices to reduce inertial residual thermal effects.

The test set up consists of a chamber capable to host the TO-8 socket for sensors, a pipeline system for the transfer of the gases from certified bottles to test chamber, a mass flow controllers (MKS mod. 647B) connected to mass flowmeters (MFCs) and a picoammeter (Keithley mod. 285) to acquire the electrical signals from the sensor. The time profile of DC current flowing through the sensor in response to various events of adsorption and desorption of nitrogen oxide or other gases was registered. A typical purging flow rate of 50 sccm was used depending on the dimension of the test chamber. A voltage of 5 V was applied to each pair of electrodes and the sensors signals, in terms of electrical

Figure 1. Electrodes and heater geometry. The detailed micrographs of the gold electrodes and of the Pt meander are evidenced

current, were acquired at different operating temperatures. The response was defined as the relative change in electrical current $I/I_0 = (I_g-I_0)/I_0$ where I_0 and I_g are the electrical current values at equilibrium in dry air and in the presence of toxic gas, respectively.

REFERENCES

[1] F. Babudri, D. Colangiuli, G. M. Farinola and F. Naso, *Eur. J. Org. Chem.* (2002), 2785-2791

[2] H. Grüniger, D. Möbius, H. Meyer, *J. Chem. Phys.*, 79 (1983) 3701-3710