

Side-Chain Role in Chemically Sensing Conducting Polymer Field-Effect Transistors

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The role of polymer side chains in conferring selectivity to a sensing organic thin-film transistor is investigated. Alkyl- and alkoxy-substituted regioregular polythiophenes are used as active layers, and a set of volatile organic compounds carrying different chemical functionalities are employed as analytes. The responses of both polymer-based transistor and quartz crystal microbalance sensors are evaluated and compared; the sensing mechanisms involving weak interactions between the analyte functionalities and the polymers' side chains are discussed as well.

Introduction

Organic-based sensing systems can offer appealing advantages such as flexible and adjustable chemical properties, room-temperature operation, and low-cost processing and fabrication.^{1–3} Most of the scientific and technological investigations on organic-based gas sensors have involved electrochemically produced conducting polymers (CPs);^{2,4–8} such films are generally amorphous with a spongelike surface morphology⁹ and result in chemiresistors exhibiting a performance level that, in most cases, is still inadequate for real applications.^{10–11} An improved performance level has been achieved with chemiresistors based on polycrystalline CP films deposited by solution casting, low-requirement vacuum deposition, or Langmuir–Blodgett techniques.^{12–17}

Recently, organic thin-film transistors (OTFTs) in a bottom-gate configuration employing polycrystalline active layers have also been successfully proposed as chemical sensors.^{18–25} Such devices can work as multiparametric sensors¹⁹ because both the on and off current variations can be used to identify chemical species. This property is derived directly from the fact that in an OTFT two distinct regimes of conductivity can be established, namely, a bulk or 3D-transport regime occurring when no gate bias is applied and 2D-transport occurring when the gate and the drain are properly biased with respect to the grounded source.^{6–28} Given the different physical nature of these two regimes of conductivity, a multiparameter response to the analyte can be obtained.¹⁹ OTFT sensors have shown extremely good response repeatability; for instance, the response is reproduced (within 2%) for 70 subsequent exposures to the analyte.²⁰ Moreover, OTFT sensors also exhibit a relative sensor response of 5–15% for 10–100 ppm analyte concentrations as well as fast response (3–5 s).²⁰

An important property of organic-based sensors is the chemical flexibility of the active layer that can be used to attain a selective device. An interesting approach, proposed by

Hierlemann et al.²⁹ and demonstrated on a set of polysiloxanes, uses side-chain functional groups to confer broad selectivity to a chemical sensor. Recently, alkyl-substituted CPs have been employed in a chemiresistor-type configuration to promote the detection of nonpolar vapors, normally a weak point of CP sensors,^{14,15} because such conductive layers are generally much more sensitive to polar substances. This strategy is also proposed to lower CPs' sensitivity to water molecules.¹⁵

In this work, we investigate the role of chemically different linear chains, used both as substituents of polyterthiophene-based sensing layers and as analyte molecules, in conferring chemical selectivity properties to the device. The polymers side groups are alkyl and alkoxy chains, and the responses of TFT and quartz crystal microbalance (QCM) devices to different organic vapors, namely, alcohols, alkanes, and ketones, are measured. The device transport properties and the sensing mechanisms involving weak interactions between the analyte functionalities and the polymers' side chains are also discussed.

Experimental Section

The polymers used in this work are poly-(3,3''-didodecyl-2,2':5',2''-terthiophene), called Poly-DT in the following discussion, and poly-(3,3''-dipentoxo-2,2':5',2''-terthiophene), named Poly-DPOT. The synthetic routes of the polymers have been published elsewhere.^{30,31} The thin films were deposited by drop casting from a saturated solution in chloroform directly over a prepatterned TFT or a QCM substrate. Films thicknesses were in the 50–60 nm range. A Danish Micro Engineering dualscope atomic force microscope (AFM) was used to study the morphology of the cast films' surfaces. Surface images were collected in tapping mode. QCM vapor-sensing experiments were carried out with a Seiko EG&G QCA917 system equipped with a homemade Teflon flow cell. Gas introduction into the measuring chamber was performed by means of two computer-controlled Brooks Smart DMFC flow meters (model 5850C). N₂ was used as an inert gas during the sensors' baseline measurements and as a carrier gas for the analytes during the signal measurement; a controlled concentration of analyte was achieved by fluxing N₂ into two consecutive sealed bottles containing the liquid analyte and mixing this vapor-saturated flux with pure N₂.

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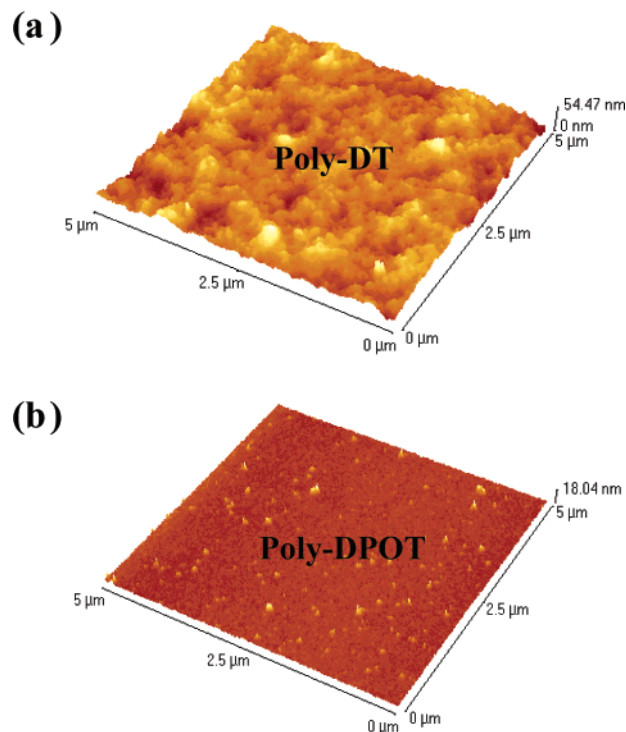


Figure 1. AFM micrographs of the polymers' polycrystalline surfaces.

Acetone and 2-propanol analytes came directly from 1000 ppm certified cylinders. The gas transfer line consisted of Teflon no-ox tubes. The TFT structure that was used is the typical bottom-gate structure^{19,20} that allows the organic layer to function both as a transistor channel and a sensing material. The structure is composed of a highly conducting silicon substrate (n-doped, $0.02\text{--}1\ \Omega/\text{cm}$) coated by a 300-nm-thick SiO_2 thermal oxide layer ($C_i = 10\ \text{nF cm}^2$). The silicon substrate with a gold ohmic contact functions as the gate (G) contact. Gold source (S) and drain (D) contacts are defined by thermal evaporation through a shadow mask on SiO_2 . The channel length is $L = 200\ \mu\text{m}$ and the width is $W = 4\ \text{mm}$. Transistor $I\text{--}V$ characteristics and the transient source-drain current are measured by means of an Agilent 4155C semiconductor parameter analyzer. Controlled concentrations of volatile organic vapors in a nitrogen flux have been realized as for the QCM measurements. The TFT sensor measurements were carried out at room temperature in an ad hoc homemade flow-through cell.³²

Results and Discussion

In Figure 1, the atomic force micrographs of the Poly-DT and Poly-DPOT film surfaces are reported; both films are polycrystalline, as is typical for alkyl chain-substituted polythiophene thin films.²² The contiguous grains composing the surfaces are larger for the Poly-DT layer than for the Poly-DPOT layer; despite this, the measured effective surface areas are comparable. The polycrystalline morphology is highly reproducible and particularly suitable to be used in sensing applications because a large surface effective area is offered to the interaction with the analyte molecules. A preliminary study of the swelling properties of such thin polycrystalline layers upon exposure to controlled atmospheres of target analytes showed that no swelling of the thin films occurred;²² a surface-type interaction such as the physisorption of the analyte molecules on the grain surface is therefore likely to take place. The physisorption of analyte molecules at the boundaries

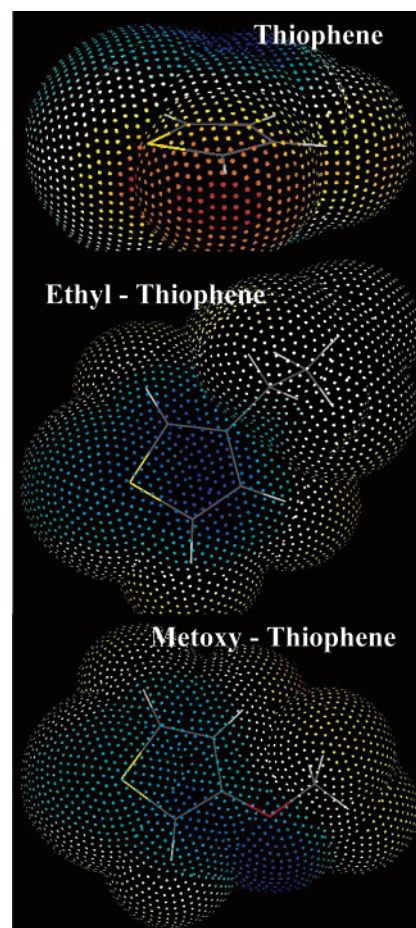


Figure 2. Color-coded representation of the electrostatic potential field associated with polythiophene, ethylthiophene, and methoxythiophene molecules. The regions at a negative potential are marked in blue, and red-orange addresses the areas at positive potential. White regions are neutral. Color intensity is an indication of field strength.

between contiguous grains is critical because it can dramatically change the film transport properties.

In Figure 2, the results of a simulation for the electrostatic potential field associated with systems chosen as models for the Poly-DT and Poly-DPOT molecules are reported. The equilibrium geometries, electrostatic potentials, and molecular dipole moments were obtained by MP2/6-31G** calculations³³ using the GAMESS-USA code.³⁴ In the pictures, the regions at negative potential, which interact favorably with positively charged species or fragments, are marked in blue. The red-orange code addresses the areas at a positive potential, and white regions are neutral. The first picture is a thiophene molecule, chosen as a model for a bare polythiophene chain. A sandwich-like charge distribution is apparent, as a red plane comprising the ring hydrogens is squeezed between two blue planes associated with the π -orbital system. This gives the system an appreciable quadrupole moment, but the dipole moment is relatively weak (modulus $\mu = 0.463\ \text{D}$). A somewhat similar situation is observed for the ethyl thiophene molecule (chosen as a model for the alkyl polythiophene) because the ethyl group is nonpolar or, in other words, almost electrically neutral. In this case, the estimated associated dipole moment is $\mu = 0.723\ \text{D}$. Note that the dangling ethyl chain lies out of the molecular plane. The methoxy-substituted thiophene differs appreciably from the ethyl-substituted thiophene both with respect to the molecular geometry and the charge distribution. Now the dangling chain lies in the molecular plane because of the favorable electron conjugation between one of the oxygen lone

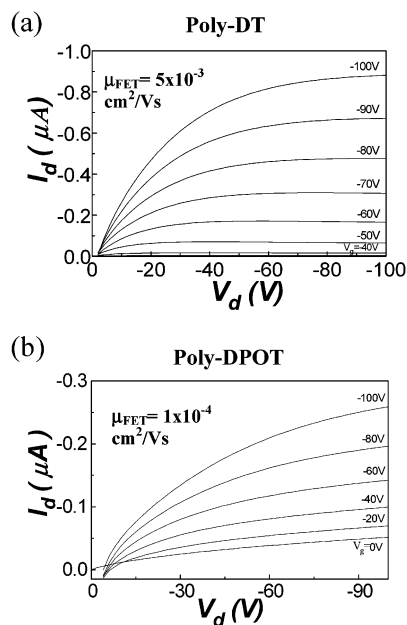


Figure 3. Current–voltage (I – V) characteristics of the Poly-DT and Poly-DPOT TFTs.

pairs and the thiophene π system. (We actually find two in-plane equilibrium geometries with the methyl groups pointing in opposite directions. We show the higher energy geometry with the largest associated dipole moment because this is the only possible conformation *in the polymer*.) This difference in the equilibrium conformation of alkyl- and alkoxy-substituted thiophenes is likely to have implications for the molecular packing and mobility in the solid state. The negatively charged region in this system extends itself from the thiophene ring to the oxygen lone pair, where the field strength increases as well; the estimated dipole moment is as high as $\mu = 1.058$ D.

To study the side-chain role in conferring selectivity to Poly-DT- and Poly-DPOT-based sensors, the analytes that were tested were alkanes and alcohols bearing alkyl chains of different lengths, namely, *n*-heptane ($\mu = 0$ D) and primary alcohols ethanol, 1-butanol, and 1-hexanol (all with similar dipole moments, with both experimental and theoretical values falling in the range of $\mu = 1.6$ – 1.7 D). Highly polar ketones such as acetone (theoretical value $\mu = 2.72$ D) as well as secondary alcohols such as 2-propanol (theoretical value $\mu = 1.67$ D) have also been tested. The last two analytes were introduced to study the influence of steric hindrance.

In Figure 3, the current–voltage (I – V) characteristics of the Poly-DT and Poly-DPOT TFTs are reported. The devices are operated in the common source configuration, and in both cases, a source-drain (I_d) current modulation is achieved with positive gate voltage (V_g) and source-drain voltages (V_d); both of the polymers are therefore p-type channel materials. Mobilities are in the 10^{-3} cm^2/Vs and 10^{-4} cm^2/Vs ranges for the Poly-DT and Poly-DPOT films, respectively. The Poly-DT film exhibits higher mobilities and much lower off currents.^{27–28} Although alkyl polythiophene materials have been extensively studied as TFT active layers, much less is known about the alkoxy materials.^{31,35–37} What has been assessed, however, is that alkoxy-substituted polymers are very stable materials in their p-doped state;^{31,35,38} this explains why the devices exhibit such a high off current. The low mobilities exhibited by both of the polymers, but in particular by Poly-DPOT, can be ascribed to the low degree of morphological and structural order of such systems. In particular, in polycrystalline films, the step deter-

mining the charge (polarons/bipolarons) mobility is the crossing of the potential barrier at grain boundaries between contiguous grains.³⁹ The low mobility of Poly-DPOT could also be an effect of charge partial localization on the oxygen of the alkoxy groups.³¹ The polycrystalline morphology of the active layer, clearly not always ideal for high-mobility TFT application, is on the contrary an advantage for sensing applications as long as a reproducible and chemically controlled nanostructured surface is obtained.

In Figure 4, the QCM responses of the Poly-DT and Poly-DPOT active layers to controlled concentrations of ethanol and 1-hexanol vapors are reported. QCM responses to the other analytes (*n*-butane, 1-butanol, 2-propanol, and acetone) have also been evaluated, and the results, reported in Table 1, will be discussed later in the text. The QCM devices were at room temperature during the measurements. It is apparent that the responses are extremely reversible and all very fast, both pieces of evidence supporting the occurrence of a weak, surface-mediated interaction. The responses, particularly that of Poly-DPOT to 1-hexanol, are linear in the investigated range, and the best extrapolated sensitivities are as good as 0.7 ng/ppm. Measured detection limits, however, are in the 50–100 ppm range.^{35–36} Exposure to all of the analytes always resulted in a mass up-take; only the Poly-DT QCM device did not respond at all to ethanol molecules.

Poly-DT and Poly-DPOT TFT responses to the same concentration of ethanol and 1-hexanol molecules are reported in Figure 5. The responses have been evaluated with an interdigitated device³⁶ housed in an in-flow cell, and the device temperature (RT) was not controlled during measurements. A working point in the saturated region of the I – V characteristics was chosen, and then the transient source-drain on-currents in the absence (baseline) and in the presence of the analyte (signal) were measured. The relative percentage responses to equal concentrations of ethanol and 1-hexanol (700 ppm) are reported in Figure 5. For the Poly-DPOT TFT exposed to both analytes and for the Poly-DT TFT exposed to 1-hexanol, a lowering of I_d occurs when the analyte flows on the TFT; this occurrence allows us to say that the mass up-take, most probably due to the physisorption of the analytes at the polymer grains, leads to an enhancement of the barriers between the grains, eventually causing the current intensity to decrease. It is interesting, from the point of view of achieving selective behavior, that no response was detected when Poly-DT was exposed to ethanol, similarly to the case of the QCM device. The other responses of both of the transistors are fair, although quite noisy; better results could have been obtained by controlling the device temperature in the 20–40 °C range. The OTFT sensor responses, however, exhibit a good degree of reversibility and repeatability, and they are also very fast. In particular, a typical response time was about 10 s (Figure 5c) or 50 s (Figure 5d), and the recovery time was 35 s (Figure 5c) or 50 s (Figure 5d). Evidently, slower response times were obtained in Figure 5d compared to those in Figure 5c. This difference could be ascribed to the different masses of the two analyte molecules, which causes a slower diffusion of 1-hexanol in the gas phase. Similar fast and reversible responses were also measured when the devices were biased at lower gate voltages, but the relative responses were appreciably lower in this case. This is preliminary evidence that an OTFT sensor response can be modulated with the gate bias, and the employment of such devices as sensing switches can be envisaged.

In Table 1, the QCM responses of the two Poly-DT and the Poly-DPOT films exposed to six different analytes, namely, a

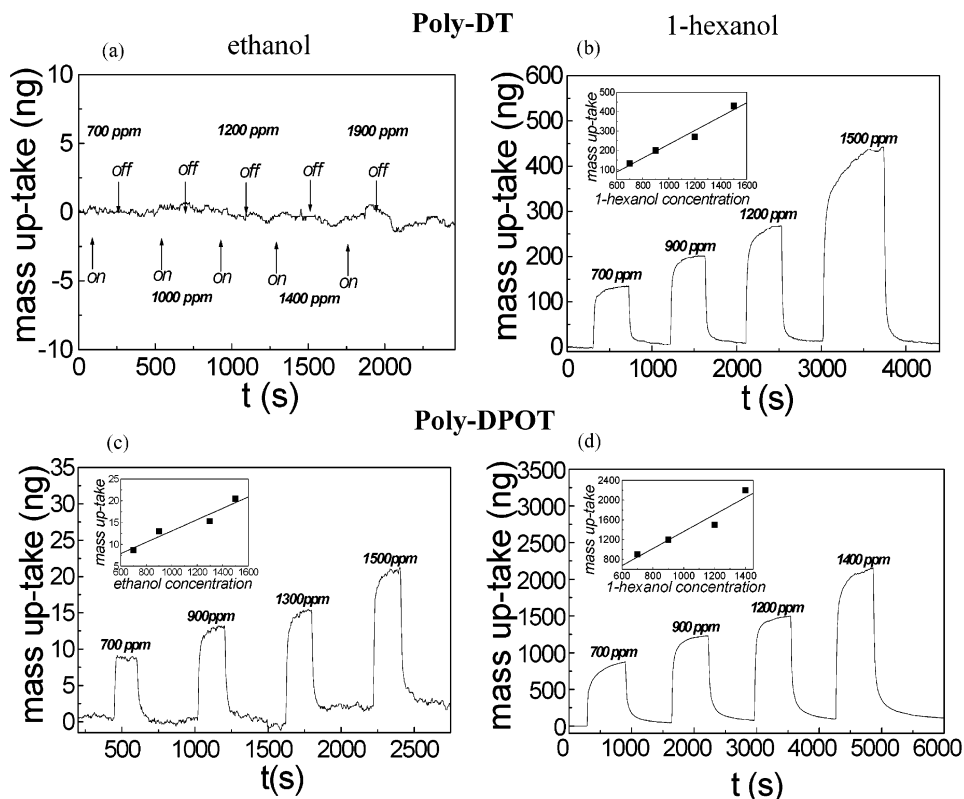


Figure 4. QCM response of the Poly-DT and Poly-DPOT sensing layers exposed to controlled concentrations of ethanol and 1-hexanol molecules in a nitrogen flow. Insets show the relevant calibration curves.

TABLE 1: QCM Responses of Poly-DT and Poly-DPOT Films to *n*-Heptane, Ethanol, 1-Butanol, 1-Hexanol, Acetone, and 2-Propanol at Fixed Concentration in a Nitrogen Flow (700 ppm)^a

	ethanol	1-butanol	1-hexanol	<i>n</i> -heptane	2-propanol	acetone
	M = 46	M = 74	M = 102	M = 100	M = 60	M = 58
	$\mu = 1.69$	$\mu = 1.66$	$\mu < 1.66$	$\mu = 0$	$\mu = 1.67$	$\mu = 2.72$
	SVP: 44	SVP: 4.4	SVP: 0.68	SVP: 35.5	SVP: 33	SVP: 185
Poly-DT ($\mu \approx 0.723$)	0	7.6	130	4	5	2
Poly-DPOT ($\mu \approx 1.06$)	10	31.8	900	7.5	11	5.5

^a M = mass in u.m.a; μ = dipole moment (D); SVP = saturation vapor pressure in Torr at 20 °C.

series of molecules bearing alkyl chains of different lengths (*n*-heptane, ethanol, 1-butanol, and 1-hexanol), as well as those of structurally different molecules such as acetone and 2-propanol are reported. The analytes are all fluxed separately on the samples at a concentration of 700 ppm in dry nitrogen. To extract the correct information on the selectivity patterns of the devices, the responses reported in Table 1 were normalized with the respect to the relevant analyte molecular mass. The saturation vapor pressures (SVPs) of the analytes are quite different; in particular, 1-hexanol is by far the less volatile substance. The mass-normalized data derived from Table 1 therefore cannot be used to derive information on the Poly-DT and Poly-DPOT selectivity patterns. As a matter of fact, in the absence of any specific chemical interaction, the partition coefficient is inversely proportional to the analytes' SVP.²⁹ The general equation proposed by R. A. Bissell et al.¹⁵ that correlates an analyte SVP (expressed in Torr at 20°C) with the concentration of the molecule in the gas phase (C_g) that is required to generate a sensor response of fixed-amplitude is the following:

$$\log\left(\frac{1}{C_g}\right) = m \cdot \log\left(\frac{1}{SVP}\right) + c \quad (1)$$

The coefficients used in the present case are $m = 0.85$ and $c =$

0.935, which result from the data obtained by R. A. Bissell et al on two differently doped regioregular poly(3',3''-didecyl-2,2'',5',2''-terthiophene) chemiresistors exposed to a series of different analytes.¹⁵

The results of the responses measured in the present work normalized by the coefficients derived from eq 1 are reported in the graphs of Figure 6. In Figure 6a, the responses of both sensors versus the analytes' associate dipole moment are reported, and in Figure 6b the same responses are plotted versus the molecular alkyl chain length (in terms of carbon units). In this second plot, the responses to acetone are not reported. In general, it is difficult in real systems to discriminate clearly between different types of weak interactions such as polar-type, dispersion-type, or polarizability because more than one process occurs simultaneously. In the present case, the Poly-DPOT and Poly-DT active layers have been chosen ad hoc to discriminate experimentally between polar-type (dipole/dipole or dipole/induced dipole) and dispersion-type (induced dipole/induced dipole) interactions. This choice was driven by the results of the Poly-DPOT and the Poly-DT chains' charge distribution simulation, showing that the former polymer bears a much stronger dipole moment, whereas the latter bears long nonpolar alkyl chains. The resulting active layers are therefore composed of domains, nanoscopic in size, bearing ad hoc chosen chemical

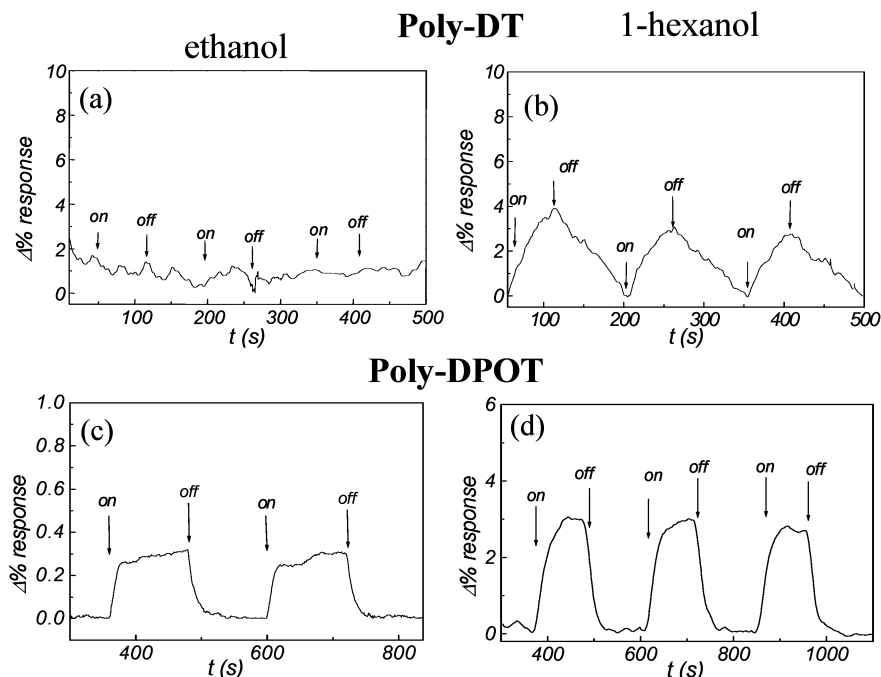


Figure 5. Relative percentage responses evaluated from the source-drain transient current variation ($V_d = -100$ V and $V_g = -40$ V) of Poly-DT and Poly-DPOT TFTs upon exposure to 700 ppm of ethanol and 1-hexanol for 2 min in a nitrogen flux. The responses of panel b were slightly lower than the saturation value ($\Delta\%$ saturation response = 5%) that could be obtained by a 5-min odor injection.

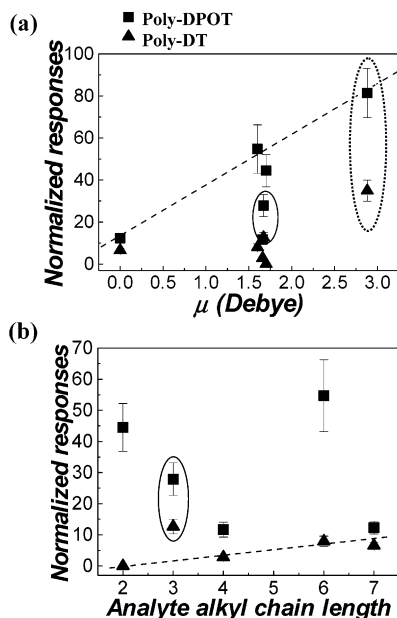


Figure 6. Normalized plots of the Poly-DT and Poly-DPOT QCM responses to a series of analyte molecules bearing alkyl chains of different lengths (*n*-heptane, ethanol, 1-butanol, and 1-hexanol) as well as to structurally different molecules such as acetone and 2-propanol. In plot a, the responses of both sensors to all of the listed analytes are reported versus the analytes' associate dipole moment; the points circled by a solid line are the responses to 2-propanol, and the points circled by a dotted line are the responses to acetone. In plot b, the responses of both sensors to all of the listed analytes except acetone are reported versus the length of the analytes' alkyl chain.

functionalities. In Figure 6a, the responses either to the alkyl chain-bearing molecules or to the acetone molecules (responses circled by a dotted line) correlate linearly very well for the polar substrate. The deviation from the trend of the responses to 2-propanol (points circled by a solid line) will be discussed later. Apparently, no clear trend is observed for the responses of the nonpolar active layer to the same analytes. Conversely, in Figure

6b, good linear correlation is found between the responses of the long alkyl chain-functionalized material and the length of the alkyl chain-bearing analytes. Similarly, the sensitivity of an oligoalkyl thiophene OTFT to an alcohol was demonstrated to increase as the length of the substituent chain on the polymer backbone was increased.²⁰ No correlation with the alkyl chain length can be seen in Figure 6b for the polar active layer. The interpretation of these results is straightforward: polar-type interactions dominate in the case of the Poly-DPOT sensor, making this device more sensitive to such substances, whereas dispersion-type interactions can be discriminated and recognized with Poly-DT devices that are also more sensitive to long alkyl chain-bearing molecules than to shorter alkyl chain alcohols. The case of 2-propanol is noteworthy; the responses to this analyte are the points circled by the solid line in the plots of Figure 6. It is apparent that these points do not follow the elicited trends. This secondary alcohol has features in common either with the alcohol analytes (functional groups) or with the acetone molecule (steric hindrance), and in this case, the polar, steric, and dispersion interactions are not distinguishable.

The conclusions drawn for the results reported in Table 1 are, in principle, extendible to the OTFT sensors because parallelism has been shown between the QCM and the OTFT sensors' responses in the case of ethanol and 1-hexanol. Besides, the model derived for the sensing mechanism gives a rationale for such a parallel trend because for both sensors the signal is originated by the analyte physisorption on the active layer.

Conclusions

Alkyl- and alkoxy-substituted polythiophene regioregular thin films show very promising properties for employment as broadly selective organic sensors. The former shows responses that are correlated to the analyte alkyl-chain length, while the latter shows responses correlated to the analyte dipole moment. These properties have been demonstrated using both OTFT and QCM sensors. An explanation for the sensing mechanisms involving surface-mediated weak interactions is given as well.

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