

Molecular Recognition for High Selectivity in Carbon Nanotube/Polythiophene Chemiresistors**

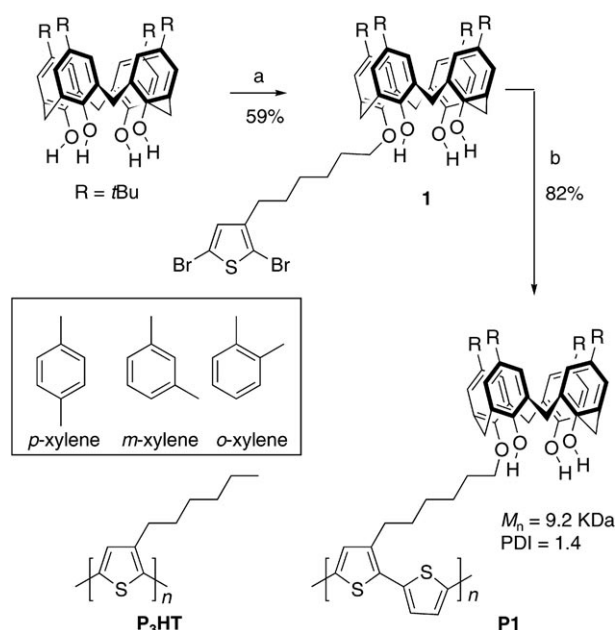
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Distinguishing structural isomers and stereoisomers is a critical and challenging task for biotechnology, the pharmaceutical industry, and environmental monitoring. One of the greatest potential applications in host–guest chemistry is to impart the necessary selectivity to sensors for the detection of these small structural differences.^[1] Although several transduction techniques have been developed for host–guest chemistry based sensors^[2] (e.g., optical, electrochemical, quartz crystal microbalance, and surface acoustic wave sensors), alternative low-cost chemiresistor devices are simple and require minimal power.

Carbon nanotubes (CNTs) are leading candidates as chemiresistor materials because of their geometric and electrical properties. In the last decade, CNT sensors have been widely explored to sensitively detect chemical^[3] and biological^[4] analytes. In these sensors, chemical modification enhances the selectivity and sensitivity, but does not contribute to the ease of fabrication.^[3c–e,4] We recently reported a single-walled CNT(SWCNT)/polythiophene-based resistor made by a greatly simplified fabrication process from a stable polymer/SWCNT dispersion.^[5] The polymer component offers great flexibility in its design and synthesis, thus enabling the incorporation of various recognition groups. We report herein a resistance sensor based upon SWCNTs wrapped with calixarene-substituted polythiophenes that is capable of a differential response to xylene isomers.

The isomers of xylene are extensively used in the chemical industry and are difficult to distinguish because of their similar physical properties such as boiling point and vapor pressure.^[6] We considered calix[4]arenes to be promising receptors^[7] to differentiate these isomers because of the shape-persistent hydrophobic binding pockets of these materials in their cone conformation. Of particular relevance is the fact that *p*-*tert*-butylcalix[4]arene can selectively extract *p*-xylene from a 1:1:1 mixture of xylene isomers.^[8] A *p*-*tert*-

butylcalix[4]arene-substituted polythiophene **P1** was synthesized by a Stille-type cross-coupling reaction between distannylated monomers and calixarene-functionalized dibrominated monomer **1**, which was prepared by monoalkylation of *p*-*tert*-butylcalix[4]arene (Scheme 1). **P1** has a number-aver-



Scheme 1. Xylene isomers, **P3HT**, and the synthesis of **P1**: a) 2,5-dibromo-3-(6-iodohexyl)thiophene, K_2CO_3 , MeCN, reflux, 24 h; b) 2,5-bis(trimethylstannyl)thiophene, $[Pd(PPh_3)_4]$, DMF/toluene (1:4), 120 °C, 48 h.

age molecular weight (M_n) of 9.2 KDa and a polydispersity index (PDI) of 1.4. To test its selectivity as a recognition group, **P1** powder was exposed to a saturated vapor of a 1:1:1 mixture of xylene isomers for 10 min and then dissolved in $CDCl_3$ (see the Supporting Information for details). The 1H NMR spectra showed that 0.38 molar equivalents of xylene isomers were adsorbed for each repeating unit of **P1**, with a distribution of 0.12/0.16/0.10 equivalents of *m*-/*p*-/*o*-xylene, respectively. As a comparison, poly(3-hexylthiophene) (**P3HT**), with the same backbone and alkyl side chain, was exposed to xylene isomers and studied in the same fashion. 0.06 Molar equivalents of xylene isomers were adsorbed for each repeating unit of **P3HT**, with an equal distribution of *m*-/*p*-/*o*-xylene. From these measurements it can be concluded that the calix[4]arene introduces a binding preference, with *p*-xylene being most favored and *o*-xylene being least favored.

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We fabricated a sensor by spin coating a stable dispersion of **P1** and SWCNTs on top of two gold electrodes (Figure 1). The polythiophene unit in **P1** is an essential dispersing element that prevents aggregation of large SWCNT bundles and forms evenly distributed percolative networks when spin coated. We measured the conductance change between the electrodes under a constant bias of 0.02 V in air as the sensory response. As a comparison, a SWCNT/**P3HT** (Scheme 1) based sensor was prepared and measured in parallel.

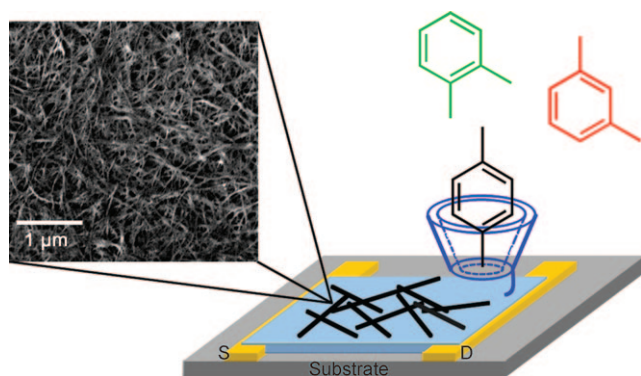


Figure 1. Schematic view of the SWCNT/**P1** sensor that selectively adsorbs *p*-xylene. A percolative SWCNT network (5 mm × 5 mm area, 30 nm thick) was deposited between two gold electrodes. An SEM image of the SWCNT network is also shown. S = source, D = drain.

As shown in Figure 2a, the SWCNT/**P1** sensor is very sensitive to the structural differences between the xylene isomers. With 40 s doses of analyte (400 ppm; dry air was used as carrier gas), we observed a conductance decrease of 12 % with *p*-xylene, 7 % with *m*-xylene, and 6 % with *o*-xylene. In contrast, the SWCNT/**P3HT** sensor showed the same response ($\approx 6\%$ conductance decrease) to all three isomers

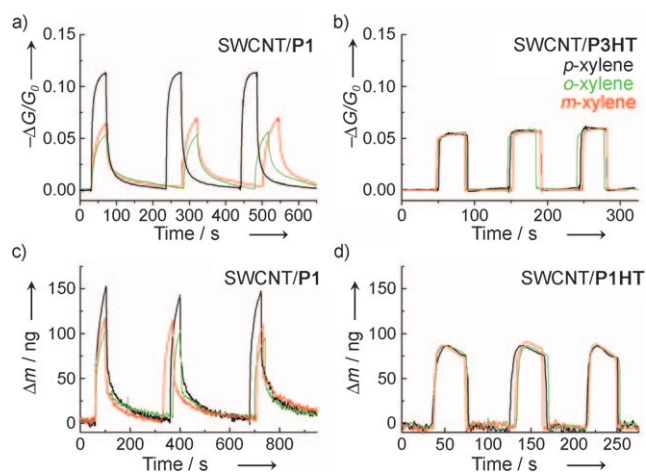


Figure 2. Conductance change ($-\Delta G/G_0$) of the a) SWCNT/**P1** and b) SWCNT/**P3HT** sensors exposed to xylene isomers (400 ppm). The weight increase (Δm) of c) SWCNT/**P1** (9.72 μg) and d) SWCNT/**P3HT** (11.0 μg) films (area: 0.39 cm^2) when exposed to xylene isomers (400 ppm) also verified the selectivity of **P1**. (Black: *p*-xylene, green: *o*-xylene, red: *m*-xylene for all plots).

(Figure 2b). We also found that replacement of the carrier gas with nitrogen did not produce any observable change in sensing response for both SWCNT/**P1** and SWCNT/**P3HT**. Additionally, the use of air with 30 % relative humidity as carrier gas at 20 °C resulted in a sensitivity decrease of only about 0.6 % without changing the selectivity (see the Supporting Information). As SWCNTs sensors are often sensitive to oxygen and moisture,^[3b] the polymer may form a protective layer^[9] that insulates SWCNTs from environmental influences.

The selectivity of **P1** for *p*-xylene was verified by a quartz crystal microbalance (QCM) study at the same analyte concentration; the SWCNT/**P1** film adsorbed more *p*-xylene than *m*- and *o*-xylene (Figure 2c), while the SWCNT/**P3HT** film adsorbed about the same quantities of all three isomers (Figure 2d). The QCM measurements are less selective for the different xylene isomers than are the chemiresistor results because a thicker film was needed to produce a sufficient signal-to-noise ratio. It is also noticeable that SWCNT/**P3HT**, in both conductance and QCM studies, has a faster recovery rate because of its weaker binding ability with xylenes.

We further monitored the adsorption phenomena by fluorescence spectroscopy, since **P1** is an emissive polymer that is sensitive to its physical environment.^[10] **P1** has a fluorescence quantum yield of 36.3 % in THF solution with absorption and emission maxima at 454 nm and 564 nm, respectively. However in thin films the absorption and emission maxima shift to 492 nm and 597 nm, respectively, which is typically observed for conjugated polymers with π aggregates and solid-state conformations that are more planar.^[10a] The emission maximum of **P1** is not shifted in SWCNT dispersions, however the quantum efficiency decreases by 75 % (to 9.0 %), which suggests that the polymer is closely associated with and quenched by the SWCNTs.^[11] To investigate the effect of xylene on **P1**, we made films of **P1** and SWCNT/**P1** in the same fashion as the sensory devices and exposed them to saturated vapors of xylene isomers. After 250 s of exposure, the fluorescence of the **P1** film increased by 56.6 %, 44.4 %, and 40.0 % for *p*-, *m*-, and *o*-xylene, respectively and the fluorescence of the SWCNT/**P1** film increased by 68.2 %, 54.8 %, and 50.2 % for *p*-, *m*-, and *o*-xylene respectively (Figure 3a). The increase in the film fluorescence indicates that the polymer underwent swelling and associated conformational changes, and confirms that more *p*-xylene is adsorbed by the film than *m*- and *o*-xylene. The fact that SWCNT/**P1** films have larger relative fluorescence intensity increases than **P1** films suggests that the polymer interactions with the SWCNT, which are responsible for the quenching, are weakened by xylene adsorption. It is notable that saturated vapors and prolonged exposures were used in the fluorescence study, thus leading to larger relative responses than our resistance measurements. The reduction of SWCNT–SWCNT interactions in SWCNT/**P1** films by xylene exposure was confirmed by Raman spectroscopy, where the relative intensity of the radial breathing mode absorptions at 265 cm^{-1} decreased by approximately 10 % when the film was exposed to *p*-xylene (see the Supporting Information). In addition, field effect transistor (FET; Figure 3b) and passivation studies (for details see the

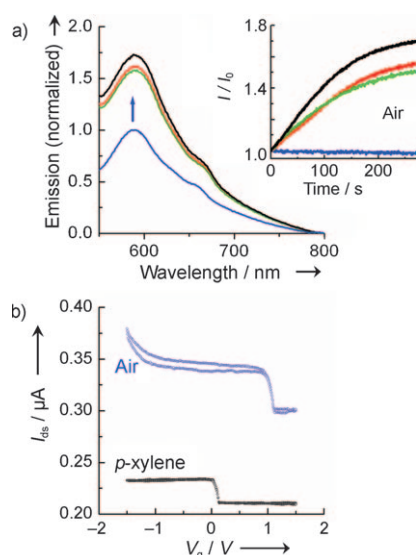


Figure 3. a) Fluorescence emission of SWCNT/P1 film in air (blue) and with exposure to saturated xylene vapors (black: *p*-xylene, green: *o*-xylene, red: *m*-xylene). Inset: fluorescence intensity changes at 597 nm (I/I_0) versus exposure time under both conditions. An excitation wavelength of 490 nm was used. b) The source-drain current (I_{ds}) versus gate voltage (V_g) of the sensor under of air (blue) and with exposure to saturated xylene vapors (only the effect of *p*-xylene exposure is shown, the same effect was found for the other isomers). The source-drain bias voltage was fixed at 0.1 V. V_g was scanned in a cycle from 1.5 V to -1.5 V.

Supporting Information), suggest that xylene transduction is the result of a combined mechanism of charge transfer and polymer conformational changes that produce greater inter-SWCNT separations.

In summary, we have developed an SWCNT/calixarene substituted polythiophene based resistance sensor. This sensor shows high sensitivity to minor structural differences in the analytes and a fast response rate. The effectiveness of this approach suggests that SWCNTs dispersed in receptor-functionalized polymers are promising candidates for low-cost, real-time, and selective chemical monitoring based on host-guest chemistry.

Experimental Section

Experimental details are given in the Supporting Information, including the synthetic procedures, adsorption experiments, dispersion methods, device fabrication processes, carrier gas effects, photo-physics of P1/SWCNT, Raman spectroscopy, and FET/passivation studies.

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