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Organic Transistor Based on Cyclopentadithiophene-Benzothiadiazole Donor-Acceptor Copolymer for the Detection and Discrimination between Multiple Structural Isomers

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Abstract. Distinguishing structural isomers is a critical and challenging task for biotechnology, chemical industry and environmental monitoring. Approaches currently available are limited in terms of selectivity. In this paper, we present a highly sensitive organic field-effect transistor (OFET) using the cyclopentadithiophene-benzothiadiazole (CDT-BTZ) copolymers as semiconductors for easy and selective detection of different families of structural isomers, as well as between different isomers within each family. High accuracy discrimination was achieved over a range of concentrations using only a single sensing parameter derived from the OFET characteristic transfer curve. As a reference, other homopolymer- and donor-acceptor copolymer-based OFET sensors were examined but did not have an equivalent sensing performance to that of the CDT-BTZ-based OFETs. Investigating the link between isomer absorption and swelling, supramolecular order and energy levels of the active layer revealed a unique effect of each isomer on the energy bands of the semiconducting polymer.

Structural isomers of volatile organic compounds play an important role in biotechnology as well as pharmaceutical and chemical industries.^[1] For example, xylene has 3 isomers, namely p-xylene, m-xylene and o-xylene, and is widely utilized in the synthesis of important chemical products, including chemical intermediates of polyesters, rubber and other polymers.^[2] Ketone and aldehyde isomers are used in a variety of applications, and are tightly connected to health issues.^[3] Indeed, volatile organic isomers have varying degrees of harmfulness at high concentrations; for example, the U.S. National Institute for Occupational Safety and Health (NIOSH) has recommended a time-weighted average permissible exposure limit of 100 ppm for xylenes, whereas for some ketones, such as 3-heptanone, it is only 50 ppm.^[4] Hence, accurate detection, monitoring and discrimination of these compounds are essential in environmental monitoring and healthcare.

Gas chromatographic mass spectrometry has long been applied for the accurate detection and quantification of structural isomers.^[5] However, it requires expensive equipment and is of limited availability. Gas sensors can be more reliable and applicable in this field since they hold promise for cheap and fast isomer detection. So far, mass sensor arrays,^[6] metal oxide semiconductor sensors,^[7, 8] chemiresistors,^[9-11] field-effect transistors (FET),^[12, 13] and cataluminescent sensors^[14] have been introduced as practical discrimination tools. Haick et al.^[13] have reported a highly selective gas sensor based on an ambipolar diketopyrrolopyrrole field effect transistor for xylene sensing. Successful detection and discrimination between isomers with <40 ppm concentrations were achieved only after applying machine learning on a combination of device parameters, including mobility (μ), threshold voltage (V_{th}) and subthreshold swing. Cross-reactive chemoresistor arrays based on gold nanoparticles or carbon nanostructures had detection and discriminative performances between ketone and aldehyde isomers, such as heptanal/3-heptanone and hexanal/2-hexanone.^[10, 11] The

discriminatory power of most of the reported sensors was largely limited to high concentrations or extreme conditions. For example, high detection limits of 10^3 and 400 ppm were reported in refs [6] and [1], respectively; 5 ppm *p*-xylene were detected using cobalt doped zinc oxide nanowire-based sensors. However, such metal-oxide-semiconductor-based sensors work only at relatively high temperatures (>400 °C), and no selectivity with regard to the other isomers of xylenes could be achieved.^[7] Other methods have used multiple cross-reactive parameters and can only discriminate between one type of isomers at a specific concentration.^[10, 11, 13] Accordingly, ***a reliable selective sensor for detecting multiple and chemically diverse isomers over a wide range of concentrations is desirable from both fundamental and practical viewpoints.***

Results & discussion

Device fabrication and performance

Herein, we report on a highly selective OFET gas sensor based on high mobility donor-acceptor copolymer (CDT-BTZ) that can discriminate between multiple isomers (derivatives of xylenes, ketones and aldehydes) over a wide range of concentrations using only one sensing parameter. OFETs based on conjugated polymers or small molecules are promising sensor platforms because they have various advantages, including high sensitivity, mechanical flexibility, and low-cost fabrication processes.^[15] CDT-BTZ was used as a semiconductor and an active sensing component in a typical OFET structure of bottom gate/bottom contact. The semiconductor material was drop-cast on the source-drain electrodes and hydrophobically-modified SiO₂ (Figure 1a,b). Figure 1c is a Scanning Electron Microscope (SEM) image of the semiconductor film composed of a very dense polymer network. The ordered packing in the solid-state contributes to the high mobility of the polymer.^[16-18] Moreover, it increases the exposed surface area, improving interactions with analytes and increasing the detection ability of sensors. Grazing-incidence scattering was used to measure the degree of supramolecular order of CDT films, and shows that the d-spacing between the chains of CDT-BTZ is ~ 3.05 nm under ambient conditions (Figure S1). Figures 1d and e present output and transfer curves of the transistor and show a typical behavior under ambient conditions. Several parameters, such as the mobility (μ), threshold voltage (V_{th}) and the source-drain currents (I_{ds}) at different gate voltages (V_g) - all of which are extracted from the OFET transfer curves - were monitored during exposure to isomers and used as sensing features. In most cases, **discrimination was achieved using only one feature.** However, by combining multiple sensing features derived from a single OFET and/or by using a pattern-recognition algorithm, chemical fingerprints for each isomer could be obtained with greater accuracy for a very wide range of concentrations.

Figure 1. Device structure and electrical performance. a) Chemical structure of the BTZ-CDT copolymer. b) A schematic showing the bottom gate/bottom contact structure of the transistor (bottom), and a photograph of the field effect transistor-based sensors with the greenish active layer above (top). c) SEM image of CDT-BTZ on octadecyltrichlorosilane (OTS)-treated SiO₂. Scale bar: 200 nm. d) Typical transfer curves at V_{ds} = -25 V (left) and output curves (e) of BTZ-CDT under N₂.

Sensor performance under exposure to organic isomers

In this report, CDT-BTZ OFETs were used to detect 7 important, but chemically different, volatile organic isomers at different concentrations (**Table 1**). These isomers were chosen for their significance in many aspects of life: xylenes, which are found in areas close to gas stations, for their relation to environmental monitoring and the necessity to make sure their concentration is under the time-weighted average permissible exposure limit of 100 ppm, and heptanal, 3-heptanone, hexanal, and 2-hexanone for their role as biomarkers of diseases in diagnosis and health monitoring.^[3, 19]

Table 1 Targeted volatile organic isomers and their physical properties.

Isomer	Chemical Structure	Boiling Point (°C)	Vapor pressure (mmHg)
p-xylene		138.6	9
o-xylene		144.4	7

m-xylene		139	9
Hexanal		129.6	11.3
2-Hexanone		127.6	11.6
Heptanal		152.8	3.5
3-Heptanone		146	4

Based on the OFET transfer curve, changes in multiple sensing parameters, such as μ , V_{th} , on-current (I_{on}), or I_{ds} at different values of V_g were extracted. The normalized parameters have different or cross-reactive responses toward the isomers, and the discrimination ability of each parameter was determined by the accuracy value, which is the proportion of true results (true positives and true negatives) of the total number of cases examined (see explanation in Section S1, Supporting Information). For simplicity, we focused on 2 parameters, μ and V_{th} , to analyze the responses and the discrimination ability. However, other parameters, such as current values, were also used. **Figure 2a-f** shows the responses of the parameters to different concentration of isomers in the range of 10 to 320 ppm for xylenes and 10 to 160 ppm for the hexanal, 2-hexanone, heptanal and 3-heptanone. The huge difference in responses to aldehydes (heptanal and hexanal) and ketones (3-heptanone and 2-hexanone) is clear in **Figure 2a-d** - over almost the whole range of concentrations. For example, as shown in **Figure 2a, b**, the effect of hexanal on the sensor between 10 to 160 ppm is much smaller compared to that of 2-hexanone allowing the discrimination between both isomers. This can be clearly seen in the box-plot demonstration as shown in **Figure S2**. Regarding xylenes, p-xylene and o-xylene have a very similar effect on the mobility, much different from the response of m-xylene. V_{th} responds differently to all the xylene isomers (**Figure 2c, d**), showing the weakest response to m-xylene. This means that p-xylene or o-xylene can be selectively discriminated from m-xylene – disregarding the concentration value - when these 3 compounds occur in a complex mixture. Moreover, the sensor can discriminate between p-xylene/m-xylene and o-xylene/m-xylene over the whole range of concentrations using only one parameter, either V_{th} or μ (**Figure S3**). The fact that we can discriminate between 2 isomers over a wide range of concentrations is highly desirable in real applications for the ability to separate/distinguish different simultaneous stimuli. On the other hand, the discrimination between p-xylene and o-xylene is only limited to specific single concentrations. The ketones and aldehydes shown in this study have a negative effect on the mobility, which might be explained by the typical swelling of the polymer because of gas uptake, increasing the distance between polymer chains and decreasing conduction.

Figure 2. Responses of CDT-BTZ to the volatile isomers over a wide range of concentrations. **a)** Normalized V_{th} and **b)** μ under exposure to 2-hexanone and hexanal in the range of 10 to 160 ppm. **c)** Normalized V_{th} and **d)** μ under exposure to 3-heptanone and heptanal in the range of 10 to 160 ppm. **e)** Normalized V_{th} and **f)** μ under exposure to xylene isomers over the range of 10 to 320 ppm. Arrows indicate the beginning of exposure to gas concentrations (ppm). Sweep cycle refers to the number of voltage sweeps from $V_g = 5$ V to $V_g = -25$ V with 1 V step.

Figure 3a-d shows the normalized responses of the parameters to different isomers. For heptanal and 3-heptanone, the difference in response is clear over the whole range of concentrations, where each compound has its own response-concentration curve. This could be due to different detection limits where aldehydes are detectable only in high concentrations compared to ketones (**Figure 3a,b**). The same behavior is found with xylenes, as p-xylene and o-xylene were detected at lower concentrations compared to m-xylenes (**Figure 3c,d**). We have also tested the evolution of responses of the sensors with time. In the previous experiments shown in **Figure 1** the exposure time was only 5 min, but here we extended this period to 30 min to study the ability of discrimination when the normalized characteristics reach equilibrium. **Figure 3e-f** shows the change in the μ and V_{th} of the sensor under exposure 160 ppm of xylenes, and **Figure 3g, h** shows the change in the μ and V_{th} of the sensor under exposure 80 ppm of heptanal and 3-heptanone. The discrimination between isomers was preserved for the whole exposure step even though it is slightly more obvious immediately at the beginning of the exposure step. This might be explained by time delays originated from the different properties

of the isomers. Noteworthy the mobility response to xylenes is positive whereas it is negative for ketones/aldehydes. This feature is very useful for the selectivity between different families of isomers. In addition, one important advantage of our CDT-BTZ sensors is straightforward discrimination directly from the value of the drain current. This leads to a simple and direct read-out with no need for further data processing, such as pattern recognition algorithms, as shown in ref [13]. Figure 3i highlights the discrimination ability between xylenes at 40 ppm using the I_{on} of the transistor. Indeed, a very high accuracy value (90%) has been obtained, which is quite unique for one-feature discrimination. To extend the study of the CDT-BTZ based sensors, we have shown the responses of the sensor to 4 mixtures (three 1:1 binary mixtures and 1:1:1 tertiary mixture) of isomers with equal total concentration on 120 ppm. Figure 3j shows the responses of I_{on} to the different mixtures showing a good discrimination accuracy of 85%. These results are consistent with the trends obtained and showed before in Figures 2 and 3 where the order of I_{on} response values ($\Delta I_{on}/I_{on}$) to the different mixtures, from high to low, was expected to be: p/o, p/m/o, m/o, p/o.

Figure 3. Normalized responses of V_{th} and μ under heptanal/3-heptanone (a, b) and xylenes (c, d). Evolution of the normalized characteristics (μ and V_{th}) under exposure to 160 ppm of xylene isomers (e, f) and 80 ppm of heptanal and 3-heptanone (g, h). The dotted lines indicate the beginning and end of gas

exposure; long exposure times were used (30 min compared to 5 min) to allow the stabilization of the response. i) Box-plot demonstration of the normalized responses of I_{on} to 40 ppm of xylene isomers. j) Box-plot demonstration of the normalized responses of I_{on} to 4 xylene mixtures (1:1 p/o, 1:1 o/m, 1:1 m/p and 1:1:1 m/p/o). k) Discrimination between all studied isomers over 20-160 ppm of hexanal, 2-hexanone, heptanal, and 3-heptanone, and 20-320 ppm for xylenes. $CV1(\mu, V_{th})$ and $CV2(\mu, V_{th})$ are obtained by a linear combination between the responses of μ and V_{th} using Discrimination functional analysis (DFA, see the experimental section for more information).

Inspired by the nature of olfactory systems, we have used arrays of cross-reactive features in conjunction with pattern recognition methods of multiple OFET parameters to obtain high selectivity toward different compounds.^[20] Using this approach, several parameters were combined to obtain optimal discriminations between isomers. In Figure 2k μ and V_{th} were used as 2 cross-reactive parameters for the discrimination between all isomers over the range of concentrations of 20-160 for hexanal, 2-hexanone, heptanal and 3-heptanone, and 20-320 ppm for xylenes. Discrimination functional analysis (DFA) was used to examine the discriminatory ability using a combination of the two parameters. New parameters were defined by this method, $CV1$ and $CV2$, which are obtained from a linear combination of $\Delta I_{on}/|I_{on}|$ and $\Delta V_{th}/|V_{th}|$. The combination of cross-reactive parameters was optimized to improve the discrimination. Figure 2k shows that the plot of $CV2$ vs. $CV1$ gives a clear separation between all groups of isomers with an accuracy value of 80%. The only limiting part, as explained before, is the discrimination between o-xylene and p-xylene. However, this large-scale discrimination between all groups of isomers is still unprecedented.

For summarizing the key merits, the device has shown exceptional discrimination ability between different types of isomers. Namely, using only one parameter, e.g., μ of the OFET, responses to xylenes were separated from one another at each specific concentration between 20-160 ppm. More importantly, responses to o-xylene and p-xylene were unprecedentedly separated from responses of m-xylene over the whole range (20-160 ppm). Ketones and aldehydes have also shown similar characteristics where sensors could discriminate between the 2 compounds over the range of 20-160 ppm using only one sensing parameter, μ or V_{th} . Furthermore, we found that the mobility response to xylenes is positive whereas for ketones/aldehydes it is negative under the range of 20-160 ppm, which makes for simple discrimination between all these families of isomers.

Investigation of the discrimination mechanism

The outstanding performance of CDT-BTZ in discriminating between multiple isomers raises a question regarding the sensing mechanism. We considered 2 types of responses: first,

swelling of the active layer or/and change in the supramolecular order because of gas absorption. Second, electrical response caused by intermolecular interaction between the analytes and the CDT-BTZ. For testing the swelling response, ellipsometry measurements were used to check thickness changes following gas absorption. The change is correlated to the amount of gas absorbed by the active layer. This experiment showed no noticeable difference between the absorption of each isomer because the changes were very similar (Table S1). From these results, we can safely infer that discrimination between isomers is mainly based on different electrical responses, but not on swelling behavior. For further examination of the effect of isomers on CDT-BTZ films, we took grazing-incidence scattering measurements to check if there was any change in the degree of supramolecular order after the absorption of gases. There were no noticeable changes in these measurements under the exposure to different isomers, which could be explained by the negligible effect of isomers on the crystalline domains because they diffuse mainly into the less compact amorphous regions. The d-spacing between the chains of CDT-BTZ was ~ 3.05 nm (Figure S1). In brief, we found no noticeable difference between the effects of isomers on the film swelling or the supramolecular order; therefore, we suggest that the different sensitivity might originate from unique intermolecular interactions between the isomers and the polymer. These interactions affect several characteristic physical parameters/properties of the sensing film, such as energy levels and work function.^{13,20} Therefore, we proceeded to investigate the electrical interactions by calculating the HOMO and LUMO levels under gas exposures using DFT. The calculations were derived from the CDT-BTZ monomer, which is supposed to provide a good approximation to the behavior of the whole polymer; however, the polymer was expected to have a more complicated response to the analytes. The HOMO and LUMO values obtained are summarized in **Table 2**. By comparing the effect of xylenes on the HOMO level, m-xylene has the most negative HOMO level, followed by p-xylenes and then o-xylene. Higher HOMO levels (more negative) lead to a higher hole injection barrier, which directly decreases the currents in the device. This is consistent with the I_{on} values obtained on exposure to different xylenes, where o-xylene has the highest I_{on} , followed by p-xylene and m-xylene; $o > p > m$. Heptanal has an outstanding effect on the energy levels of CDT-BTZ compared to the other isomers; however, this was not correlated to any corresponding responses of the sensing parameters. In addition, the optimized molecular structure of the CDT-BTZ and its complexes with the other isomers obtained showed different electron density distribution (**Figure 4**). The optimized structures show that isomers preferably interact with the benzothiadiazole (BTZ) group, whereas the cyclopentadithiophene (CDT) group, which is shielded with long aliphatic chains, is less affected (Figure 4). The long aliphatic chains might interrupt the intermolecular interactions with isomers or prevent them from reaching the CDT group. In general, each isomer has its

own electrical effect on the orbital energies and the electron density distribution of CDT-BTZ chemical structure, leading to a unique fingerprint for each compound.

Table 2 HOMO, LUMO, and bandgap energies of the CDT-BTZ and its complexes with the different isomers.

	CDT-BTZ	CDT-BTZ + heptanal	CDT-BTZ + 3-heptanone	CDT-BTZ + m-xylene	CDT-BTZ + p-xylene	CDT-BTZ + o-xylene
LUMO (eV)	- 2.778	- 2.573	- 2.854	- 2.882	- 2.883	- 2.826
HOMO (eV)	- 5.240	- 5.196	- 5.301	- 5.322	- 5.299	- 5.287
E _g (eV)	2.462	2.623	2.447	2.44	2.416	2.461
ΔE _g (eV)		0.161	-0.015	-0.022	-0.046	-0.001

Figure 4. Electron-density distribution of CDT-BTZ and its complexes with different isomers, optimized by the B3LYP/3-21G method.

Empirical comparison with other polymers

To support our conclusion regarding the unique selectivity of CDT-BTZ, we compared its performance to other polymeric semiconductors including: poly(3-hexylthiophene) (P3HT),

poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene] (PBTTT), poly[2,5-(2-octyldodecyl)-3,6-diketopyrrolopyrrole-alt-5,5-(2,5-di(thien-2-yl)thieno[3,2*b*]thiophene)] (PDPP-DTT) and poly[3,6-dithiophene-2-yl-2,5-di(2-octyldodecyl)-pyrrolo[3,4-*c*]pyrrole-1,4-dione-alt-naphthalene] (PDPP-TNT); Figure S4 gives more details). These polymers introduce different modes of conjugation ranging from homopolymers to donor-acceptor copolymers. Similar sensors were fabricated, using the same method and structure, and then exposed to the gas concentrations in the same experimental systems. The discrimination accuracy of the sensors was evaluated for comparison with those obtained with CDT-BTZ. Figure 2j shows that CDT-BTZ has a very high discrimination accuracy of 98% between xylenes at 40 ppm; however, the other polymers (P3HT, PBTTT, PDPP-DTT and PDPP-TNT) failed to show any discrimination ability even after using the best combination of parameters as obtained by the DFA method (Figure S5). In addition, the discrimination ability between isomers over the range of 10-160 ppm was examined; Table S2 summarizes the discrimination accuracy values of CDT-BTZ and the other polymers. The other polymers also reveal some kind of discrimination between ketones and aldehydes over the range of 10-160 ppm; however, the accuracy values obtained are much lower than those of the CDT-BTZ copolymer. For the xylenes, the other polymers, compared to CDT-BTZ, gave lower discrimination ability between the pairs of *m*-xylene/*o*-xylene and *p*-xylene/*m*-xylene over the range of 10-160 ppm, using μ as a sensing parameter. The highest accuracy was obtained with PBTTT; 85% and 80% for *m*-xylene/*o*-xylene and *p*-xylene/*m*-xylene, respectively. However, V_{th} responses to isomers were similar and gave very low accuracies of <60%. Similar to the performance of CDT-BTZ, discrimination between *p*-xylene and *o*-xylene was challenging. Compared to the other tested polymers, CDT-BTZ contains a functional benzothiadiazole group that is not shielded by aliphatic side chains, and contains 2 nitrogen sites that might have a significant role in interactions with isomers, leading to a different sensing behavior compared to normal thiophene groups found in the other polymers. Therefore, in order to test this assumption, we also examined the sensitivity of another TBT containing polymer, poly(diketopyrrolopyrrole-thiophene-benzothiadiazole-thiophene) (PDPP-TBT, See Figure S4), toward the studied xylenes, ketones, and aldehydes. This polymer did not show any remarkable selectivity toward xylenes while the selectivity to hexanal, 2-hexanone, heptanal, and 3-heptanone was comparable to CDT-BTZ (Table S2). The superior performance of CDT-BTZ might be originated from the specific combination between electron-deficient and electron-rich groups which introduce differently interacting sites along the polymer backbone. The role of the backbone interacting sites and functional groups needs further investigations to better understand the molecular origin of discrimination between isomers.

We have introduced a new gas sensor based on an OFET fabricated from a donor-acceptor polymer semiconductor with high charge carrier mobility. This device allows selective

discrimination between multiple isomers over a wide range of concentrations. The high discrimination ability could, in principle, originate from different electrical interactions, such as doping and trapping, between the isomers with the polymer backbone, especially the electron deficient benzothiadiazole, giving a unique sensing fingerprint for each isomer. These conclusions were justified by DFT calculations that pointed to distinct polymer-isomer interactions (mainly on the benzothiadiazole moiety). In addition, the performance of CDT-BTZ was compared to those of other semiconductors to support the role of the monomer structure in this high selectivity. This work is mainly focused on sensor performance and its discrimination ability between isomers. Further work is also needed to better understand the main interaction between isomers and CDT-BTZ. Moreover, the different trends in responses to ketones/aldehydes and xylenes, where xylenes led to increased currents whereas the other gases showed decreased values, could not be explained based on the DFT results alone. From the viewpoint of practical sensing, the superior selectivity obtained in this work, which is not just limited to only one type of isomers, is unprecedented compared to other reported devices. Therefore, further studies on the sensing and selectivity mechanism down to the molecular or atomic level are desirable. Nevertheless, this sensor will be a great alternative to current complicated or limited isomer discrimination methods, even more so because it can be applied for environmental monitoring and non-invasive diagnostic technologies.

Experimental Section

Materials: P3HT (regioregular, average M_n 54,000–75,000, electronic grade, 99.995% trace metals basis) was purchased from Sigma-Aldrich. CDT-BTZ (C_{16} , M_n 28,000), PBTBT (C_{14} , $M_n > 50,000$), (M_n 76,323), PDPP-TNT (M_n 63,750), and PDPP-TBT (M_n 60200) were synthesized as reported previously in literature.^[16-18, 21-26]

Fabrication of the FET Sensor: CDT-BTZ OFETs were prepared on silicon wafers capped with 300 nm thermal oxide. A Ti/Au (10/200 nm) bottom-gate electrode was deposited by electron beam evaporation. A total of 49 pairs of circular interdigitated source and drain Au (300 nm) electrodes were prepared using photolithography and electron-beam evaporation. The outer diameter of the circular electrode area was 3000 μm . The gap between the 2 adjacent electrodes (channel length) and the width of each electrode were 25 and 5 μm , respectively. The silicon wafers were treated with plasma and immersed in octadecyltrichlorosilane (ODTS)/toluene solution (60×10^{-3} M, 20 mL) for 10 h. Finally, CDT-BTZ films were deposited on the OTS-treated substrates by drop-casting using a CDT-BTZ solution (2 mg mL⁻¹) in chloroform. The surface morphology of the CDT-BTZ film was characterized by SEM.

FET-Sensor Measurements: CDT-BTZ OFET sensor was loaded into a stainless-steel chamber of ~300 cm³. For the exposure of pure vapors, a computer-controlled bubbler was filled with the corresponding liquid, and then N₂ was bubbled through. The resulting gas mixture (N₂ and organic vapor) was diluted to obtain the desired concentrations. For the preparation of mixtures, the outputs of several bubblers were mixed together and diluted as needed. Vacuum was used as a baseline between gas exposure cycles. The total flow rate was kept at 5 L min⁻¹ during the experiment. Source-drain current I_{ds} versus gate voltage V_g measurements (swept between 5 and -25 V with 0.5 V steps and -25 V constant source-drain voltage, V_{ds}) were carried out using a Keithley 2636A system SourceMeter and a 3706 system Switch/Multimeter. Extraction of the sensing parameters following the FET measurements is given in detail in section S1 (Supporting Information).

DFT Calculations: B3LYP/3-21G simulator was used to calculate the optimized molecular structure, and the HOMO and LUMO energies of complexes of CDT-BTZ with each isomer under vacuum.

Discriminant function analysis: DFA analysis used JMP 10 software (SAS Institute, Inc.). DFA finds linear combinations of sensing features that separate 2 or more classes of objects. In binary classification, DFA predicts membership in 2 categories based on known continuous sensing responses. For the discrimination between all isomer groups, CV1 and CV2, a linear combination of $\Delta I_{on}/|I_{on}|$ and $\Delta V_{th}/|V_{th}|$, were used. $CV1 = 0.631 * \Delta I_{on}/|I_{on}| - 2.073 * \Delta V_{th}/|V_{th}|$, and $CV2 = 0.502 * \Delta I_{on}/|I_{on}| + 0.995 * \Delta V_{th}/|V_{th}|$.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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The table of contents entry: A highly-sensitive donor-acceptor copolymer cyclopentadithiophene-benzothiadiazole (CDT-BTZ) based organic field-effect transistor (OFET) can easily and selectively detect multiple types of highly similar structural isomers at low ppm levels. This includes xylene isomers, ketones and aldehydes, such as heptanal and 3-heptanone, which are highly reliable for many industrial applications. Robust discrimination is obtained between different families as well as between the isomers within each family.

Keywords: organic field-effect transistor, donor-acceptor copolymers, gas sensor, isomers, xylenes

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Organic Transistor Based on Cyclopentadithiophene-Benzothiadiazole Donor-Acceptor Copolymer for the Detection and Discrimination between Multiple Structural Isomers

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Supporting Information:

Organic Transistor Based on Cyclopentadithiophene-Benzothiadiazole Donor-Acceptor Copolymer for the Detection and Discrimination between Multiple Structural Isomers

Muhammad Khatib, Tan-Phat Huynh, Jiaxing Jeccy Sun, Felix Hinkel, Klaus Müllen, and Hossam Haick*

Experimental methods

Spectroscopic ellipsometry measurements: the sample was placed into a 5 ml liquid cell and exposed to different gases (160 ppm) before measurements were taken. The thickness of CDT-BTZ was measured by using a spectroscopic phase-modulated ellipsometer (V-VASE, J. A. Woollam Co., Inc., USA). Ellipsometric spectra were recorded over a range from 300–1000 nm with an incidence angle of 70°. A 3-phase Si/SiO₂ (100 nm)/polymeric film model was used to extract the thickness of the organic layer.

Grazing-incidence measurement: the sample was placed in a sealed graphite chamber and exposed to different gases (160 ppm) before the measurements were taken. The sample inside the graphite chamber was measured using Rigaku SmartLab 9kV (45 kV, 150 mA), SC-70 detector, Cu K α (PRINT WITH GREEK LETTER) 1.54 Å radiation, angle range of 0 ° <2 θ <20° (omega = 0.6).

S1. Extraction of the sensing parameters

Hole-mobility was calculated using Eq. 1 in the saturation regime:

$$Eq. 1 \quad I_{ds} = \frac{\mu C_i W}{2L} (V_g - V_{th})^2,$$

where I_{ds} is the drain current in the saturated regime, C_i is the dielectric capacitance per unit area, W and L are the wide and length of the FET channel, respectively, and V_g and V_{th} are the gate and threshold voltages, respectively. V_{th} was calculated by extrapolating the linear fit of $(|I_{ds}|)^{1/2}$ vs. V_g plot to $(|I_{ds}|)^{1/2} = 0$.

S2. Responses and accuracy calculation

Using the normalized curves for each OFET parameter (e.g. V_{th} or μ), the response is calculated according to the following equation:

$$Eq. 2 \quad R = 100 * \frac{F_{MP} - F_{BL}}{|F_{BL}|},$$

Where R is the responses in %, F_{MP} is the middle point of the peak (marked with black circles in the figure below). F_{BL} is any baseline point (marked with stars in the figure below).

Accuracy evaluation

The accuracy value describes the ability to discriminate between groups of gases. After plotting the responses of the sensor to different gases, if separate clusters (that correspond to each group of gases) are obtained, this means that the sensor can discriminate between the gases. By assigning a specific range of values to each group, the accuracy can be calculated by the portion of points found in the correct corresponding range. The highest accuracy is obtained when having completely separated clusters.

Figure S1. Grazing-incidence scattering measurements on exposure to different gases.

Figure S2. Responses of CDT-BTZ to hexanal and 2-hexanone over the range from 10 to 160 ppm. a) Normalized V_{th} and b) μ under exposure to hexanal and 2-hexanone in the range of 10 to 160 ppm. Box-plot demonstration of the responses of V_{th} (c) and μ (d) to different concentrations (10-160 ppm) of hexanal and 2-hexanone. Accuracy values are given in Supplementary Table S2.

Figure S3. Box-plot demonstration of the responses of V_{th} (a) and μ (b) to different concentrations (10-160 ppm) of the 3 xylene isomers (2 repetitions of each concentration). Accuracy values are given in Table S3.

Figure S4. Chemical structures of the other polymers used in the empirical study.

Figure S5. Box-plot demonstration of CV (V_{th} , μ) responses of the other polymers to xylene isomers at 40 ppm. CV gives the best combination between V_{th} and μ that results in the highest discrimination ability.

Table S1. Thickness gain of CDT-BTZ in response to different isomers at 160 ppm.

Gas	Thickness Gain (%)
Heptanal	9.6 ± 1.8
Heptanone	10 ± 1.0
p-xylene	15.6 ± 1.7
m-xylene	15.7 ± 1.3
o-xylene	15.2 ± 2.1

Table S2. Summary of the accuracy values for the discrimination ability of the semiconducting polymers to 20-160 ppm targeted isomers.

Isomer	Feature	Accuracy %					
		CDT-BTZ	P3HT	PBTTT	DPP DTT	PDPP TNT	PDPP TBT
p-xylene / m-xylene	V_{th}	96	<60	<60	<60	<60	<60
	μ	93	75	80	<60	70	<60
	I_{on}	87	80	80	<60	<60	<60
p-xylene / o-xylene	V_{th}	<60	<60	<60	<60	<60	<60
	μ	<60	<60	<60	<60	<60	<60
	I_{on}	<60	<60	<60	<60	<60	<60
o-xylene / m-xylene	V_{th}	96	<60	<60	<60	<60	<60
	μ	100	70	85	<60	65	<60
	I_{on}	90	75	80	<60	<60	<60
Hexanal / 2-Hexanone	V_{th}	90	90	90	80	85	<60
	μ	85	75	80	75	65	90
	I_{on}	80	77	80	<60	70	92
Heptanal / 3-Heptanone	V_{th}	93	70	75	73	70	<60
	μ	90	80	85	76	90	87
	I_{on}	93	80	83	70	85	90