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Organic field effect transistors based on poly(3-hexylthiophene) and Cu^{II} tetraphenylporphyrin composite were investigated as sensors for detection of vapors of nitrobased explosive compounds, viz., 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 2,4,6-trinitrotoluene (TNT), and dinitrobenzene, which are also strong oxidizing agents. Significant changes, suitable for sensor response, were observed in transistor "on" current (I_{on}) and conductance (S) after exposure. A similar device response was, however, not observed for oxidizing agents such as benzoquinone and benzophenone. The Fourier transform infrared spectrometry experiments supported the results, where exposure to RDX and TNT vapors resulted in a significant shift in IR peaks. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3049130]

In recent years, semiconducting materials based on organic molecules and polymers have been researched extensively for their electrical properties as active materials, mainly as organic field effect transistors (OFETs).[1–3] Low-cost integrated circuits with these OFETs have been demonstrated with polymer materials.[4] The application of organic polymers for sensing of various gases has also been reported in literature.[5–8] The alkoxy-substituted polyterthiophene thin film based organic transistors have been demonstrated to work as alcohol sensors with sensitivities as good as 0.7 ng/ppm.[9] Also, a humidity sensor based on 1,4,5,8-naphthalene-tetracabooxylic-diannhydride has been reported.[10] Use of sexithiophene in organic thin film transistor has been reported for detection of explosives, specifically 2,4,6-trinitrotoluene (TNT).[11] The possible use of metalloporphyrins for detection of explosives (mainly TNT)[12–14] and toxic gases such as NO$_2$ (Refs. 15 and 16) has also been reported earlier. In this paper, the use of OFET is demonstrated as a sensor for nitrobased explosive compounds. Two parameters were employed for sensing; (i) drain Current (I_{on}) and (ii) linear-region conductance (S). A poly(3-hexylthiophene) (P3HT) composite was employed as the organic semiconducting layer.

Three terminal OFETs were used for performing the experiments, using the bottom contact configuration. Figure 1 shows the schematic of device structure as well as the chemical structures of P3HT and Cu^{II} tetraphenylporphyrin (CuTPP). A heavily doped (0.01–0.02 Ω cm) *n*-type silicon substrate was used as a gate electrode for the OFETs. 100 nm thick thermally grown SiO$_2$ ($C_{ox}=34.5$ nf/cm^2) acted as a gate dielectric. Interdigitated source-drain electrodes of Ti/Au (10 nm/50 nm) were patterned using the lift-off photolithography technique. The channel length of the devices was varied from 30 to 70 μm with the widths varying from 17 050 to 24 850 μm. The substrates were treated with hex-

amethyldisilazane (HMDS) by spinning at 500 rpm for 5 s followed by 4000 rpm for 30 s, with the baking done at 120 °C for 8 min. Enhancements with HMDS treatment have been reported in general for OFETs (Ref. 17) and, in particular, for *n*-type devices, possibly due to the passivation of interfacial traps.[18,19]

The composite of P3HT (from Sigma Aldrich) and CuTPP (synthesized as reported in literature[20]) was dissolved in chloroform (3 mg/ml) and spin coated at 1000 rpm for 45 s to form a thin layer of organic material. The prepared devices were cured at 90 °C for 1 h in normal ambient conditions. Characterizations were also done in normal ambient conditions using Keithley 2400 SMU, Keithley 2602 system source meter, 617 electrometer, and Agilent E3631A power
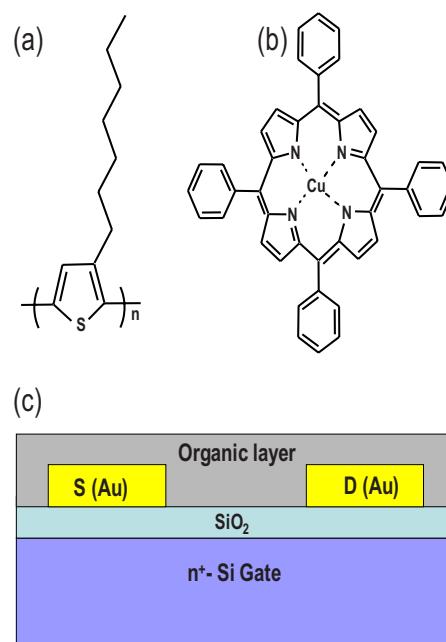

FIG. 1. (Color online) (a) Chemical structure of P3HT. (b) Chemical structure of CuTPP. (c) Structure of OFET.

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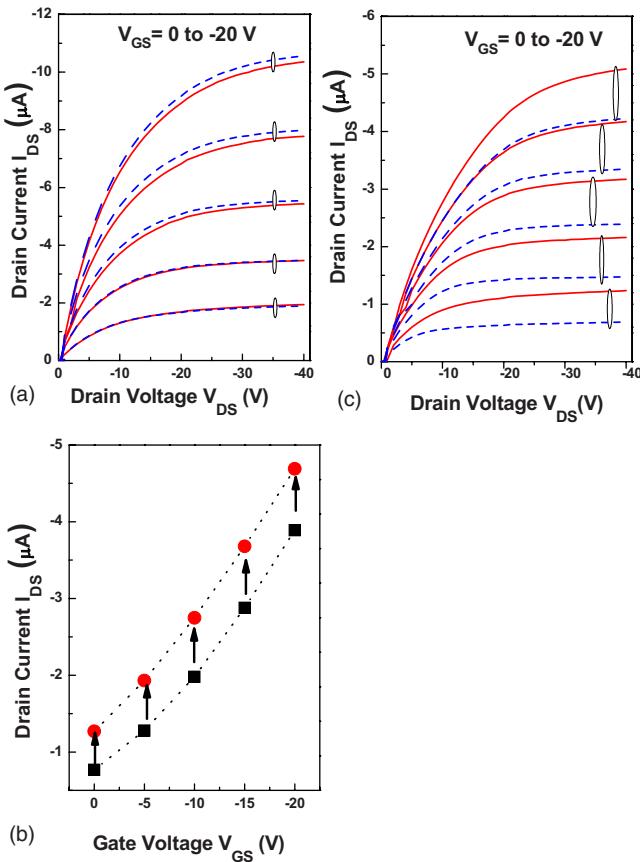
FIG. 2. (Color online) (a) I_{DS}-V_{DS} for P3HT based OFET for various values of V_{GS}, the dotted curve showing the response without RDX vapors and the solid curve with exposure to RDX vapors. (b) I_{DS}-V_{GS} plot at $V_{DS}=-40$ V, wherein rise in current after exposing to RDX vapors is indicated. ■ shows the current without exposure to RDX while the red dot shows the current with exposure. (c) I_{DS}-V_{DS} characteristics for P3HT+CuTPP composite OFET for various values of V_{GS}. The dotted curve shows the response without RDX vapors and the solid curve with exposure to RDX vapors.
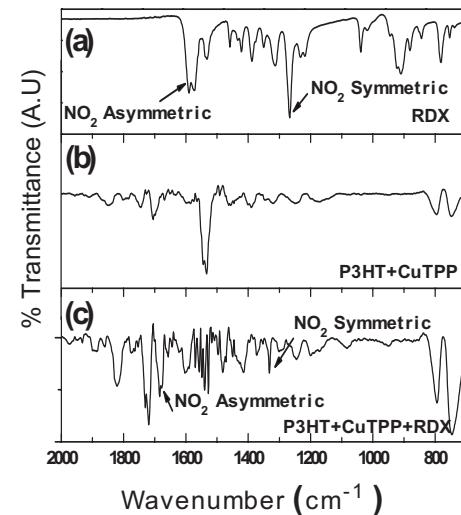

FIG. 3. Fourier transform infrared (FTIR) spectra, wherein (a) is of pure RDX, (b) is for P3HT+CuTPP, and (c) is for P3HT+CuTPP after exposing to RDX vapors. Shifts in peaks are clearly seen in part (c) indicating the binding of RDX molecules to the polymer composite.

supply. *I-V* measurements were done for various gate (0, −5, −10, −15, and −20 V) and drain voltages (0 to −40 V). The 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) vapors were generated by heating solid RDX at 120 °C with a carrier gas flow rate of 20 SCCM (SCCM denotes cubic centimeter per minute at STP). To ensure exposure to saturated vapors, all the sensors were kept in a closed box through which RDX vapors were passed continuously for 30 min. *I-V* measurements for each sensor were taken before and after exposure of RDX vapors.

Initially, only P3HT was used as the organic layer. Figure 2(a) shows the output characteristics (I_{DS}-V_{DS} at various V_{GS}). The results clearly indicate that the RDX vapors did not have any considerable effect on the I_{DS} of the sensing devices. Change in conductance of the film, measured in the linear region of operation, was found to be negligible (1%–2%). A plausible explanation could be the inability of the nonaromatic RDX molecular interaction with the π-cloud of P3HT. However, it is interesting to note that appreciable changes in I_{on} (15%–20%) and conductance (8%–10%) were observed on exposure to TNT vapors. The improved sensitivity to TNT could be due to the strong π-π interactions between the electron-deficient aromatic TNT molecule and the P3HT polymer. TNT molecules are strong acceptors and hence when they are in the vicinity of P3HT, due to the binding with metalloporphyrins, they can cause a change in

the charge carrier characteristics, due to a change in concentration, mobility, or because of different charge carriers becoming more active, resulting in a change in the conductance.

Equation (1) was used to obtain conductance,[2] where the values of field effect mobility (μ) and threshold voltage (V_T) were obtained by a linear fit between the I_D-V_{GS} data measured at $V_{DS}=-2$ V and Eq. (2), expression for drain current of a transistor in the linear region.[21]

$$S = \mu C_{ox} \frac{W}{L}(V_{GS} - V_T), \tag{1}$$

$$I_{DS} = \frac{1}{2}\mu C_{ox} \frac{W}{L}\left[(V_{GS} - V_T)V_{DS} - \frac{1}{2}V_{DS}^2\right], \tag{2}$$

$$\sigma = Nq\mu, \tag{3}$$

where μ is the field effect mobility, C_{ox} is the capacitance per unit area of the gate dielectric [F/cm²], V_T is the threshold voltage, W (width) and L (length) are the dimensions of the semiconductor channel defined by the source and drain electrodes of the transistor, σ is the film conductivity, N is the total number of carriers per unit area in the film, and q is the electron charge.

Motivated by previous studies on the formation of molecular complexes between metalloporphyrins and various acceptors,[22] the same experiment was now repeated with P3HT and CuTPP as the organic layer. Figure 2(c) shows the output characteristics in this case. The solid and dotted lines represent the *I-V* characteristics with and without exposure to RDX vapors, respectively. Figure 2(b) shows the change in drain current measured at different gate voltages. This comparison clearly indicates that there is a significant rise in the drain current after exposure to RDX vapors. Significant change (10%–15%) was also observed in the conductance of the film. Superior sensor response in this case could be due to the well-known strong tendency to form coordinate bonding between the metalloporphyin molecule and the nitrogroup[22] as well as the π-stacking between the porphyrins and aromatic rings of the P3HT polymer.[12] The RDX molecule, now bound to the porphyrin cavity, is able to come

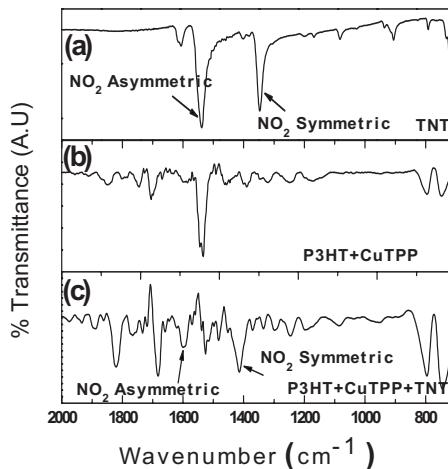FIG. 4. FTIR spectra, wherein (a) is of pure TNT, (b) is for P3HT+CuTPP, and (c) is for P3HT+CuTPP after exposing to TNT vapors. Shifts in peaks are clearly seen in part (c) indicating the binding of the TNT molecules to the polymer composite.

in close proximity to the π-stacked porphyrin and polymer thereby enabling the RDX molecules to improve the film conductance by removing excited electrons from the π-system of the polymer.

The effect of the RDX molecules on the P3HT/CuTPP polymer film is supported by the shift in IR peaks. The major shifts were in the peaks corresponding to asymmetric NO_2 stretching (from $1572/1590$ to $1676/1688$ cm^{-1}) and symmetric NO_2 stretching (from 1266 to 1332 cm^{-1}), as shown in Fig. 3. Similar behavior was also observed in the case of TNT exposure (Fig. 4) which resulted in peak shifts from 1347 to 1414 cm^{-1} and from 1538 to 1599 cm^{-1}, corresponding to symmetric NO_2 stretching and asymmetric NO_2 stretching, respectively.

In order to address the issue of selectivity, we exposed the P3HT and CuTPP based transistors to various analytes. We selected nitrobenzene (NB), dinitrobenzene (DNB) and TNT—all nitrobased explosive compounds, along with benzoquinone (BQ) and benzophenone (BP)—non-nitro, nonexplosive compounds. Characterization and analysis of experimental results obtained for all the analytes have been summarized in Table I. It is observed that the overall response was significant only for nitrobased explosive compounds (with the exception of NB). The sensor response to the other analytes (BP, BQ, and NB) was almost negligible. As explained in the case of RDX, strong interactions between metalloporphyrins and the nitrogroup could be responsible for the selectivity toward nitrobased compounds. The

metalloporphyrins have large binding constants for nitroaromatics relative to free-base porphyrins,[22] and our experiments were in agreement with this behavior. On the other hand, the poor sensor response to strongly oxidizing BQ could be due to the low binding strength (K_b), leading to low polymer-quinone interactions.[23] In order for the sensor to respond to a given analyte, the analyte has to be electron deficient and also stay within a close proximity of P3HT (it should bind with the metalloporphyrins in the present case). In the case of BQ and BP, although they are as good oxidizing agents as TNT and RDX, due to the low binding constants they might not bind with the receptors (metalloporphyrins in our case) and hence could not be detected. So the detection mechanism involves binding and matching of the oxidizing power. In the case of TNT and RDX both of these were positive and therefore the sensor shows a much higher sensitivity compared to BQ and BP.

In conclusion, P3HT and organic composite (CuTPP) based OFETs were demonstrated as the sensors for nitrobased explosive compounds. I_{on} and conductance were shown to be the parameters that can be used for the recognition of the molecular species. While the P3HT film was shown to be responsive specifically to the TNT, the addition of CuTPP to the organic film gave improved sensitivity to various nitrobased explosive compounds (TNT, RDX, and DNB).

TABLE I. Sensor parameter response (conductance and I_{on}) to various oxidizing nitro- and non-nitrobased compounds.

IUPAC name	E_{red} [a] (V)	Change in conductance (S)	Change in I_{on}
1,3,5-trinitro-[1,3,5] triazinane (RDX)	⋯	8%–10%	18%–22%
2,4,6-trinitrotoluene (TNT)	−0.7	10%–15%	20%–25%
1,3-dinitrobenzene (DNB)	−0.9	5%–8%	10%–15%
Nitrobenzene (NB)	−1.15	<1%	2%–4%
1,4-benzoquinone (BQ)	−0.5	<1%	2%–3%
Benzophenone (BP)	−1.6	1%–2%	2%–3%

[a]Reference 23.

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