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Trifluoromethyl ketone P3HT-CNT composites for chemiresistive amine sensors with improved sensitivity

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ABSTRACT

Chemiresistive sensors, wherein conductivity is changed by exposure to analytes, are widely used in various disciplines and in our daily lives. Carbon nanotubes (CNTs) are excellent materials with exceptional conductivity, and polymer/CNT composites have been extensively deployed in chemiresistive sensors. To improve sensitivity, we herein report the covalent functionalization of poly(3-hexylthiophene)s (P3HTs) with highly electrophilic trifluoromethyl ketones, referred to as TFMK-P3HT, and its composite with CNT and amine sensing were investigated. The synthesis was begun with the bromination of commercial P3HT, followed by a lithium-halogen exchange reaction and subsequent quenching with trifluoroacetic anhydride, producing TFMK-P3HT. Homogeneous CNT networks with TFMK-P3HT were confirmed by atomic force microscopy (AFM). The sensing of three representative amines with TFMK-P3HT/CNT showed four times higher sensitivity than P3HT/CNT samples. The sensors were selective to amines and less responsive to competitive gas species such as alcohols and H_2S. The sensitivity improvements of the TFMK-P3HT sensor were maintained in humid conditions. This work suggests a facile synthetic method to improve the sensitivity of CNT-based chemical sensors and provides an effective gas sensor platform for the selective detection of amine gas.

1. Introduction

Sensor technologies have provided us with invaluable tools for our daily lives, with notable examples of glucose sensors and pregnancy tests. Numerous sensing systems have been developed, and their operations are centered on a variety of scientific principles and related instrumentation including chemiresistivity [1,2], fluorescence [3,4], nuclear magnetic resonance spectroscopy (NMR) [5], surface-enhanced Raman scattering (SERS) [6], and smartphone-based wireless sensors [7,8]. Among these examples is a chemiresistive sensor that shows superiority owing to high sensitivity, digital readout, low cost, low operation power, and portability [9]. They are mainly composed of conducting materials that transport charged carriers as well as receptors that interact with analytes. Exposure to an analyte changes the conductivity of the active materials, and a simple measurement of resistance through an I-V curve generates digitalized data that allow us to confirm the existence, identity, and even the concentration of an unknown species [9].

Amine sensing is of critical importance because amines are generally considered to be toxic [10,11]. They are found in many critical situations, such as food spoilage and environmental pollution. In the former, biogenic amines (e.g. putrescine, cadaverine, and trimethylamine) are emitted upon the spoilage of meat and fish[12,13] with the concentration of more than 60 ppm [14], and in the latter, atmospheric ammonia gas as well as nitrogen oxides (NOx) are hazardous and thus imperative to detect [15]. According to Occupational Safety and Health Administration (OSHA), a recommended exposure limit of NH_3 is 25 ppm for employees working eight hours a day. Besides the toxicity, amines are used as a disease biomarker since some patients exhale volatile organic compounds (VOCs) that are characteristic of certain diseases (e.g. trimethylamine for acute heart failure and fatty liver disease) [16]. In this sense, the development of sensitive amine sensors would be able to facilitate non-invasive disease diagnosis.

Carbon nanotubes (CNTs) have been extensively employed as active materials in chemiresistive sensors since the first report in 2000 [17].

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The molecular wires feature an extended π-conjugated surface and a long persistent length (typically a few to hundreds of microns, depending on literature as well as CNT types) [18], thereby providing fast transport of charged carriers and thus presenting high conductivity as well as sensitivity in chemical sensing. Comprehensive applications of CNT sensors are found in environmental monitoring [19], food and agriculture [20,21], biosensors [22–25], and national security [26]. In the field of amine sensing, bare CNTs could detect NH_3, resulting in the decreased conductivity owing to the electron transfer from Lewis-basic NH_3 to p-type semiconducting CNTs [17]. To improve sensitivity and selectivity, CNTs have been formulated with other materials such as metal oxides and acids [27–29], or covalent modification of CNTs have been employed to attach chemical moieties that can selectively interact with amines [30]. Although these strategies were shown to be efficient, there are several issues that are currently unresolved. The employed metal oxides inherently have limited functional groups that can be appended, and CNT chemistry is restricted to aromatic double bonds and/or carboxylic acids (present after oxidation). It is also challenging to characterize the covalent CNT functionalization since CNTs are insoluble in organic solvents and thus routine analytical techniques such as NMR, chromatography, and mass spectrometry are rarely applied. In addition, the covalent modification results in the transformation of sp^2 carbons to sp^3 carbons, wherein electronic coherence and conductivity are destroyed [31].

To overcome these issues, non-covalent CNT modification can be employed. In particular, π-conjugated polymers have been used as efficient CNT wrappers through enthalpic π-π interactions to form a stable dispersion and can append synthetic receptors to impart selectivity [32–34]. Some conjugated polymers can disperse CNTs with specific chiral indices and even extract semiconducting SWCNTs due to the strong coherent interaction [35], and P3HT/CNT composites are known to have exceptional oxidative stability [36]. Besides these advantages, the functionalized conjugated polymers can be characterized by analytical techniques, thereby enabling the determination of the exact molecular structures, unveiling polymer-analyte interactions, and thus providing structure-property relationships for improved sensitivity and selectivity in chemical sensing. However, in some cases, the polymer/CNT composites may have lower sensitivity because polymers partially block the potential physisorption sites of the CNTs that can also sense analytes.

In this work, we report a method that improves the sensitivity of polymer/CNT chemiresistive amine sensors through the chemical modification of polymers. To achieve this, we were interested in the incorporation of trifluoromethyl ketone (TFMK) as an electrophilic site on π-conjugated polymers. The degree of electrophilicity can be indirectly evaluated by a hydration reaction of ketones. As depicted in Fig. 1a, the hydration of acetone is unfavorable, placing the equilibrium mostly on the reactant side ($K_{eq} \sim 10^{-3}$). A remarkable equilibrium shift by one billion (from 10^{-3} to 10^{6}) is observed when two methyl groups in acetone are replaced with two trifluoromethyl groups, forming hexafluoroacetone (Fig. 1a) [37]. Inspired by this equilibrium shift, we hypothesized that the reactivity to amines, or sensitivity, could be enhanced if TFMK groups are installed on P3HT (Fig. 1b). Indeed, having synthesized the polymer and fabricated a chemiresistive sensor with the polymer/CNT composites (Fig. 1c), we observed that TFMK-based polymer/CNT sensors revealed enhanced sensitivity toward primary, secondary, and tertiary amines in ambient and humid environments (vide infra).

2. Materials and methods

2.1. Polymer synthesis

2.1.1. Br-P3HT

This polymer was synthesized by following the literature procedure or slight modification thereof [38,39]. To the flame-dried Schlenk flask, P3HT (300 mg, 1 equiv., 1.80 mmol based on a repeat unit, M_n 21, 600 g/mol, M_w/M_n = 2.74) was dissolved in chloroform. *N*-bromosuccinimide (387 mg, 1.2 equiv., 2.17 mmol) was added portionwise, and the entire mixture was covered with aluminum foil. The mixture was stirred for 12 h. Then the temperature was increased to 50 °C and stirred for 2 h. Upon cooling to room temperature, the mixture was washed three times with saturated sodium bicarbonate (aq) and subsequently three times with water. The combined organic layer was added dropwise to methanol to obtain yellow precipitates. After filtration, the precipitates were dried in vacuo at 50 °C. 81% yield (360 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.71 (br, 2 H), 1.57 (br, 2 H), 1.28 (br, 6 H), 0.87 (br, 3 H) (GPC: M_n 32,300 g/mol, M_w/M_n = 2.53).

2.1.2. TFMK-P3HT

This polymer was synthesized by following the literature procedure or slight modification thereof [39]. To the flame-dried Schlenk flask, Br-P3HT (330 mg, 1 equiv., 1.35 mmol based on a repeat unit) was dissolved in THF (60 mL) and placed in a dry ice/acetone bath. *n*-BuLi (3.3 mL of 1.6 M in hexane, 4 equiv., 5.3 mmol) was added and stirred for 15 min. Trifluoroacetic anhydride (1.9 mL, 10 equiv., 13.5 mmol) was added. The mixture was further stirred at − 78 °C for 15 min and subsequently at room temperature for 4 h. The mixture was then added to methanol to induce precipitation. The precipitates were filtered, thoroughly washed with methanol, and dried in vacuo at 50 °C. ^{1}H NMR

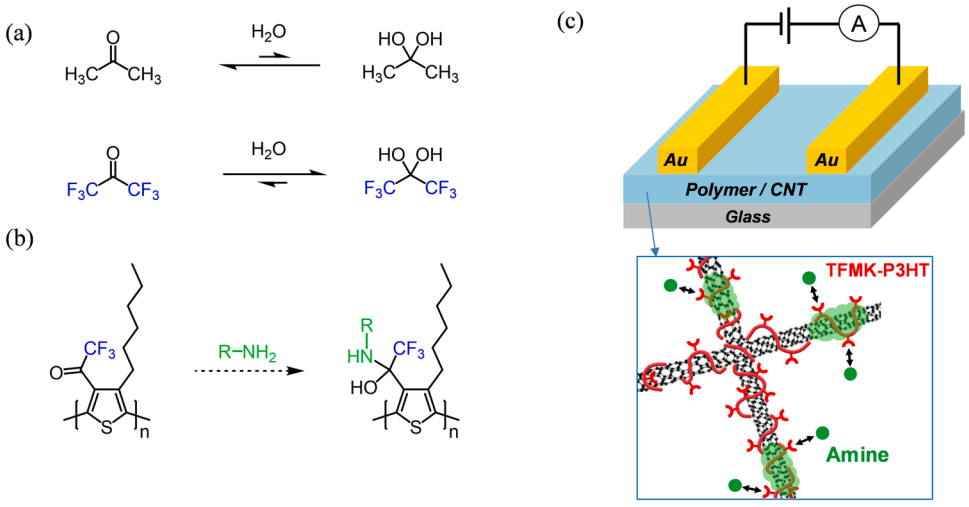

Fig. 1. Overview of this work. (a) The equilibrium of acetone hydration to form a geminal diol is at the left side ($K_{eq} \sim 10^{-3}$). However, hexafluoroacetone possesses a highly electrophilic sp^2 carbon, giving rise to the equilibrium shift to the geminal diol ($K_{eq} \sim 10^{6}$). (b) Based on this equilibrium shift from electrophilicity modulation, P3HT with trifluoromethyl ketone at the 4-position was synthesized to improve sensitivity toward amine sensing. (c) This TFMK-P3HT mixed with single-walled carbon nanotube (SWCNT) was used as an active layer of the chemiresistive sensor.

(400 MHz, $CDCl_3$) δ 2.60 (br, 2 H), 1.57 (br, 2 H), 1.25 (br, 6 H), 0.88 (br, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ − 74.27 (br). GPC: M_n 20, 500 g/mol, $M_w/M_n = 2.93$.

2.2. Polymer/CNT composites and AFM measurement

P3HT and TFMK-P3HT were dissolved in an organic solvent with a concentration of ~ 2 mg/mL (in the case of TFMK-P3HT, the polymer was not entirely soluble. Hence, it was dissolved with a small amount of chloroform to obtain concentrated samples and diluted for use. The exact concentration (~ 2 mg/mL) was calculated by measuring the undissolved polymer mass). CNT was dispersed in the same organic solvent with a concentration of ~ 2 mg/mL and mixed with the polymer solution, thereby achieving a 1:1 ratio (by weight) of the CNT and the polymer (either P3HT or TFMK-P3HT). The mixture of polymer and CNT was sonicated for 1 h and centrifugated at 9000 rpm for 15 min. A clear supernatant containing the individually dispersed CNTs wrapped by the polymer was then collected. For AFM sample preparation, a silicon wafer (p-type, LG Siltron, Korea) with 1 cm × 1 cm was washed with acetone and isopropanol, after which the remaining solvent was removed with N_2 blowing. The washed wafer was cleaned in an UV ozone cleaner for 30 min. The polymer/CNT dispersion (80 μL) was placed on the wafer, followed by spin-coating with 3000 rpm for 90 s

2.3. Device fabrication and amine sensing

The resistor-type sensor devices were fabricated to monitor changes of electrical properties of P3HT/CNT and TFMK-P3HT/CNT in response to gas exposure. First, glass substrates were cleaned by sonication in acetone and isopropyl alcohol for 15 min each, followed by 365 nm UV irradiation for 10 min. Then, P3HT and TFMK-P3HT solutions blended with CNT in chloroform (1:1 wt%) were deposited on the substrates by drop-casting in an ambient condition. Source-drain gold electrodes (50 nm) were thermally deposited under a vacuum of 4.5×10^{-6} Torr at a deposition rate of 0.5 Å/s. For electrical characterizations, current-voltage curves of the devices were measured at room temperature (25 °C) using a Keithley 4200 semiconductor parameter analyzer before and after exposure to analyte vapors. In sensing experiments with relative humidity 60% and 80%, corresponding water (1.38 μL and 1.84 μL, respectively) was vaporized in the 0.1 L sensing chamber, assuming that water vapor is an ideal gas.

3. Results and discussion

The synthetic procedures to install TFMK proceeded with two steps beginning with commercially available poly(3-hexylthiophene) (P3HT) [39]. First, P3HT underwent electrophilic bromination at its 4-position using *N*-bromosuccinimide (NBS) (Fig. 2a). This bromination was achieved quantitatively, confirmed from the ^1H NMR spectrum in which the 4-position proton signal at 6.98 ppm completely disappeared (Fig. 2b). Second, this Br-P3HT (**2**) was mixed with *n*-BuLi at − 78 °C to execute a lithium-halogen exchange reaction, which forms lithiated P3HT, followed by an in situ substitution reaction with trifluoroacetic anhydride (Fig. 2a). The resulting polymer is referred to as TFMK-P3HT (**3**). The ^{19}F NMR spectrum of **3** indicated a tall, relatively broad peak at − 74 ppm (Fig. 2c), which demonstrated the successful incorporation of trifluoromethyl ketone groups on P3HT (the ^1H NMR spectrum of **3** was included in Supporting Information). During the experiments, it is recommended that trifluoroacetic anhydride be injected all at once, in spite of heat generation, to avoid the potential crosslinking between lithiated P3HT (nucleophilic) and the instantly formed TFMK-P3HT (electrophilic). Indeed, we observed a decrease in solubility after this reaction; however, it still had enough solubility to perform in the subsequent experiments. GPC analysis revealed the molecular weight of 22 kDa (P3HT), 32 kDa (Br-P3HT), and 21 kDa (TFMK-P3HT), although the TFMK-P3HT molecular weights indicated batch-to-batch differences.

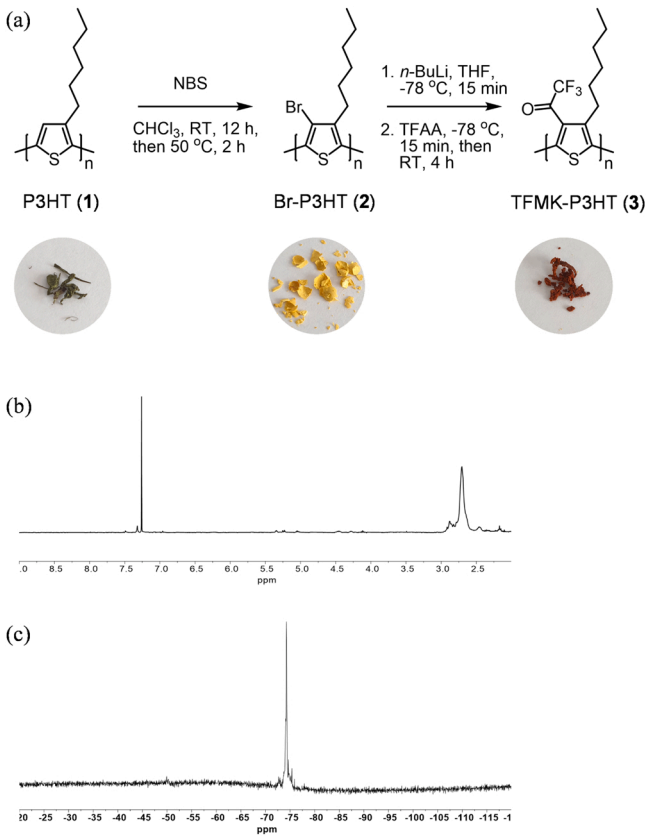

Fig. 2. Polymer functionalization and characterization. (a) P3HT (**1**) was brominated with N-bromosuccinimide. This Br-P3HT (**2**) reacted with n-butyllithium through lithium-halogen exchange, followed by quenching with trifluoroacetic anhydride to append trifluoromethyl ketone at the 4-position of P3HT. The colors of each polymer were shown in the insets. (b) The ^1H NMR spectrum of Br-P3HT (**2**). A proton peak at 6.98 ppm disappeared, indicative of quantitative bromination. (c) The ^{19}F NMR spectrum of TFMK-P3HT (**3**). A relatively broad fluorine signal at − 74 ppm was observed.

This difference is perhaps attributed to the rate of reagent injection and the reaction scale. GPC traces are included in Fig. S1.

The photophysics of three polymers (P3HT, Br-P3HT, and TFMK-P3HT) in solution were examined with UV–vis and fluorescence spectroscopy (Fig. 3). Br-P3HT indicated a large blue-shift in both absorption

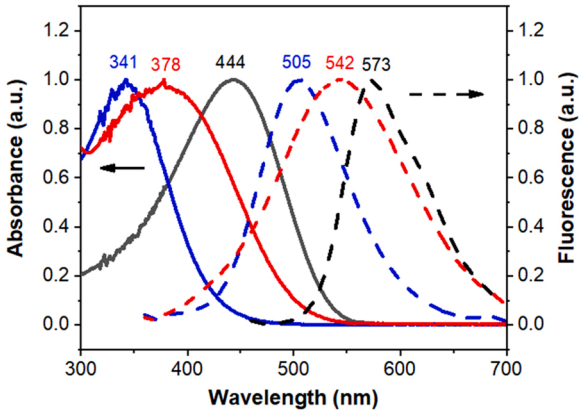

Fig. 3. Absorption and fluorescence spectra of P3HT derivatives (black: P3HT; blue: Br-P3HT; and red: TFMK-P3HT). Owing to the large size of the bromine atom, the polymer chain of Br-P3HT is highly twisted, causing a large blue shift relative to P3HT. TFMK is also large in size; however, the degree of a blue shift is modest in comparison to Br-P3HT.

and emission spectra owing to the steric bulk of a large bromine atom that would cause the polymer backbone to be highly twisted. Notably, TFMK-P3HT also showed a large hypsochromic shift in reference to P3HT, but the degree of the shift was less than that of Br-P3HT. It is believed that the TFMK may have rotational freedom and be adjustable to keep the polymer backbone moderately planar (low in energy), whereas bromine has a spherical shape that cannot be spatially adaptable due to its steric bulk, resulting in a highly twisted polymer backbone. The Stokes shifts of P3HT, Br-P3HT, and TFMK-P3HT were 129 nm, 164 nm, and 164 nm, respectively. Generally, a large Stokes shift is expected for polar fluorophores dissolved in polar solvents [40], which was the case for Br-P3HT and TFMK-P3HT.

Next, the polymer/CNT composites were prepared. Briefly, the polymer (P3HT or TFMK-P3HT) and CNT were mixed with a 1:1 wt ratio in an organic solvent and sonicated. After centrifugation, the supernatant was collected (Fig. 4a). In order to visualize the CNTs, the solution was spin-coated on a silicon wafer, and AFM images with a non-contact mode were taken (Fig. 4b). The sample surface was smooth enough to take well-resolved AFM images; however, it was noted that the drop-casted samples were too rough to obtain clear AFM images. As shown in Fig. 4b, the CNTs were evenly dispersed on the wafer, and the amount of CNTs were sufficient to form an interconnected network that would enable the charged carriers to flow. However, the amount of CNTs in TFMK-P3HT appeared to be lower than the one from P3HT dispersion. It is well-known that a planar polymer backbone can form efficient wrapping around CNTs due to facilitated π-π interactions (i.e., nanowire formation), whereas a twisted backbone cannot form the nanowire, which may result in the less dispersion of CNTs in the case of TFMK-P3HT [41].

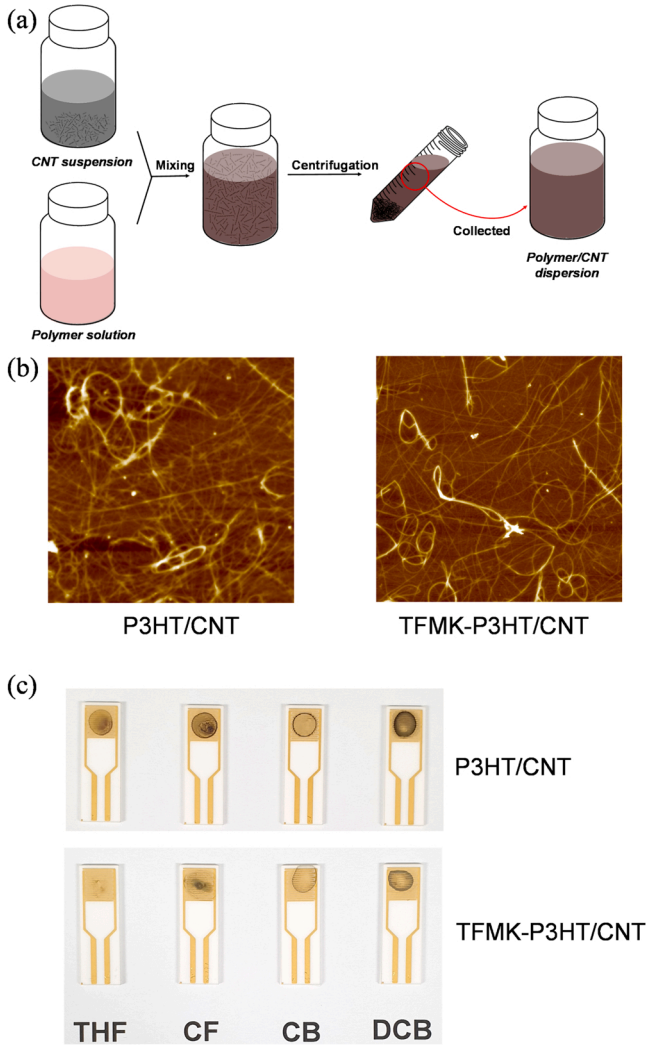

Fig. 4. Preparation of polymer/CNT composites and their characterization. (a) CNT and polymer (1:1 by weight) in an organic solvent were mixed, sonicated, and centrifugated. The supernatant which contains CNTs wrapped by the polymers was collected. (b) AFM images (5 μm × 5 μm) of the polymer/CNT composites. Both P3HT/CNT and TFMK-P3HT/CNT showed well-dispersed CNT networks. (c) The photographs of the drop-casted samples prepared in different solvents on interdigitated gold electrodes.

Solvent effects on the degree of polymer/CNT dispersion were investigated in the following four different solvents: tetrahydrofuran (THF), chloroform (CF), chlorobenzene (CB), and *o*-dichlorobenzene (DCB). Fig. 4c displays the drop-casted polymer/CNT composites in different solvents on interdigitated gold electrodes (IGEs). DCB was able to disperse both P3HT/CNT and TFMK-P3HT/CNT effectively and formed thick films. DCB is known to form sufficient dispersion of CNT without any additives [42], and we also observed this phenomenon even in the absence of the polymers. The resistances (measured by a multimeter) of both P3HT/CNT and TFMK-P3HT/CNT indicated a few ohms, implying a high concentration of CNTs. In CF, CB, and THF, we still gained a satisfactory dispersion for both polymer/CNT samples. However, the P3HT/CNT generally indicated more CNT dispersion as a result of planar backbone conformation, and the resistances were near hundreds, thousands, and tens of thousands of ohms for CF, CB, and THF, respectively. The TFMK-P3HT/CNT films indicated higher resistances (up to one order of magnitude) in the same condition for each solvent.

Attributed to the excellent dispersion of TFMK-P3HT/CNT, we applied this film to chemiresistive amine sensing. We employed three different amines based on their varying number of substituents, i.e., ethylamine, diethylamine, and triethylamine. For the sensing experiment, liquid amines were fully vaporized at room temperature in a 100 mL-size chamber in an ambient condition for saturation when relative humidity (RH) in the measurement day was 45% (the picture of the sensing setup is presented in Fig. S5). Voltage was applied to plot an I-V curve whose slope was to be a reciprocal of a resistance. The resistance change, or sensitivity which is defined as the ratio of $R_{Analyte}$ (resistance with an analyte) to R (resistance without the analyte), is summarized in Fig. 5. As can be seen from Figs. S6–S8, resistances of both P3HT/CNT and TFMK-P3HT/CNT sensors were increased in response to amine vapor. However, the degrees of the increases were significantly different. The P3HT/CNT sensors (grey in Fig. 5) indicated minimal resistance changes upon the exposure to amines, whereas the

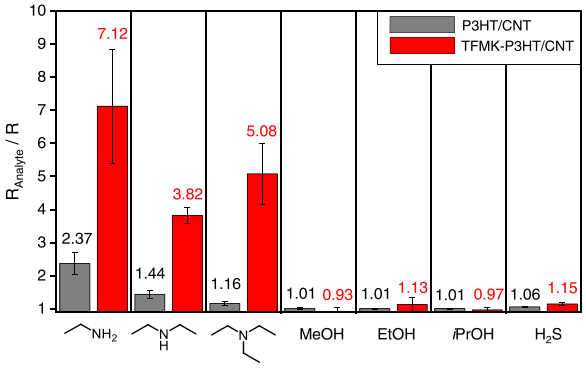

Fig. 5. Sensing data. $R_{Analyte}$ and R are resistances in the presence and absence of analyte, respectively. Grey and red bars are the resistance ratios for P3HT/CNT and TFMK-P3HT/CNT, respectively. The measurements were repeated three to five times and the averaged R values were indicated. The red bars clearly indicated the improved sensitivity for all amines. The degrees of improvement were 3.00 fold (ethylamine), 2.65 fold (diethylamine), 4.36 fold (triethylamine). The sensor was not responsive to alcohol vapors and H_2S, indicating the selective, improved detection of amines from the TFMK-P3HT/CNT sensor.

TFMK-P3HT/CNT sensors (red in Fig. 5) exhibited much higher resistance changes (upto 9 times). The average sensitivity improvements were 3.00 times, 2.65 times, and 4.36 times for ethylamine, diethylamine, and triethylamine, respectively, which clearly demonstrated the effect of TFMK groups on the amine sensing. This improvement was also observed in different concentrations of ethylamine sensing (Fig. S9). Comparing the sensitivity improvements across amines was challenging in our study since each amine has different vapor pressures (ethylamine (870 mmHg), diethylamine (180 mmHg), and triethylamine (50 mmHg)). In order to explore other analytes and evaluate the selectivity, three alcohols and hydrogen sulfide (H_2S) were employed (Figs. 5 and S10). The values of $R_{Analyte}/R$ in the four analytes were close to one in both sensors, indicating that the sensitivity improvements were negligible. As control experiments, chemiresistors prepared from pristine CNT dispersion without polymers in *o*-DCB (1 mg/mL) were exposed to ethylamine, diethylamine, and triethylamine, and the $R_{Analyte}/R$ values were merely from 1.03 to 1.18 (Fig. S11).

The reversibility of the sensors was further examined using ammonia gas (NH_3, 100 ppm) owing to its volatility and facile desorptivity in an ambient atmosphere (Fig. S12). Upon the exposure to NH_3, both P3HT/CNT and TFMK-P3HT/CNT sensors exhibited increased resistances, wherein TFMK-P3HT/CNT indicated a much higher increase in resistance as described above. When the sensors were exposed to air, followed by NH_3, the P3HT/CNT sensors indicated relatively reversible responses, whereas the TFMK-P3HT/CNT sensors showed more irreversible behaviors. We believe that NH_3 molecules could interact with TFMK-P3HT in a chemical way (i.e., possibly through a tetrahedral intermediate or imine formation), while NH_3 molecules would interact with P3HT/CNT in a physical way (i.e., physisorption).

We then examined the effect of moisture on this sensitivity improvement (Fig. 6). Moisture is known to complicate chemical sensing data and often deteriorate the sensing capability [43,44]. For example, different levels of RH induced disparate sensing responses in the differentiation of SO_2 and NO_2 [45], and RH below 10% was required to achieve the differentiation of volatile organic compounds (VOCs) in CNT-based sensors [46]. To check the sensitivity improvement in humid environments, we performed the sensing experiment in RH 60% and 80% with ethylamine and the data were shown in Fig. 6 (raw data in Figs. S13 and S14). We found that the TFMK-P3HT/CNT sensors indicated higher sensitivity than the one from the P3HT/CNT in both RH conditions (3.06 times in RH 60%; and 3.38 times in RH 80%). However, overall sensitivities were decreased when they were compared to the ambient condition, indicating that the humidity is still a concern in our chemical sensing. It is believed that the pre-existing water molecules could interrupt the interaction between the amine and polymer/CNT, but the electrophilic TFMK-P3HT still can capture amines more efficiently than P3HT in the humid environment, which is consistent with our hypothesis.

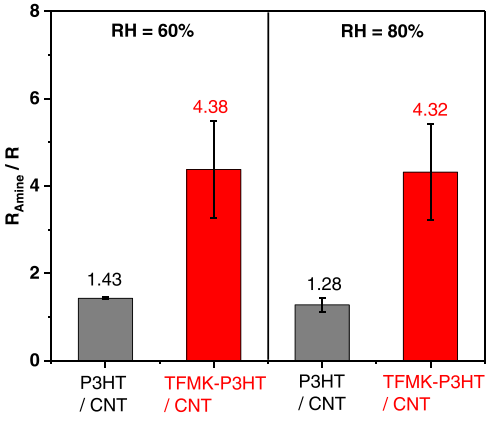

Fig. 6. Ethylamine sensing data in RH 60% and RH 80%. In both cases, the sensitivities were improved about three times in TFMK-P3HT/CNT (3.06 times in RH 60%; 3.38 times in RH 80%).

These improved sensitivities of TFMK-P3HT/CNT sensors can be explained in several ways [47]. In general, the current decrease was observed due to the charge trapping effect of amine molecules [48,49]. The difference between TFMK-P3HT and P3HT may be attributed to the fact that amines would have reacted more efficiently with TFMK-P3HT than P3HT due to the increased carbocationic character as expected. This improved reactivity may have given rise to the higher swelling of TFMK-P3HT/CNT composites, which can slightly separate the individual molecular wires and thus decrease carrier tunneling exponentially, which is referred to as an inter-CNT effect (Fig. 7a). Along with this inter-CNT effect, it is possible that charge (holes in CNT) trapping owing to the lone-pair electrons of amines could be facilitated in the presence of TFMK, thereby decreasing the hole mobility, which is called an intra-CNT effect (Fig. 7b).

4. Conclusions

In this study, we report the functionalization of commercially available P3HTs to attach highly electrophilic trifluoromethyl ketone (TFMK) and the fabrication of chemiresistive amine sensors exhibiting improved sensitivity. The polymer functionalization includes bromination, lithium-halogen exchange, and a substitution reaction with trifluoroacetic anhydride. This TFMK-P3HT had a slightly twisted polymer backbone due to the steric congestion, while the degree of the twist was modest in comparison with brominated P3HT. TFMK-P3HT was able to wrap CNTs efficiently, producing a transparent composite solution that had a sufficient concentration of CNTs for sensing experiments. Chemiresistive sensor devices were prepared with TFMK-P3HT/CNT and P3HT/CNT. Exposure to primary, secondary, and tertiary amines exhibited that TFMK-P3HT/CNT sensors showed sensitivities three to four times higher than the one from P3HT/CNT samples in both ambient and humid conditions. The sensitivity improvements were selective to amines, not alcohols and H_2S. We believe that the amine sensing strategy that employs electrophilic functional groups can be widely adopted for sensing other nucleophilic molecules that have significance in chemistry, biology, and materials science.

CRediT authorship contribution statement

Yeong Gyu Kim: Methodology, Investigation. **Byeong M. Oh**:

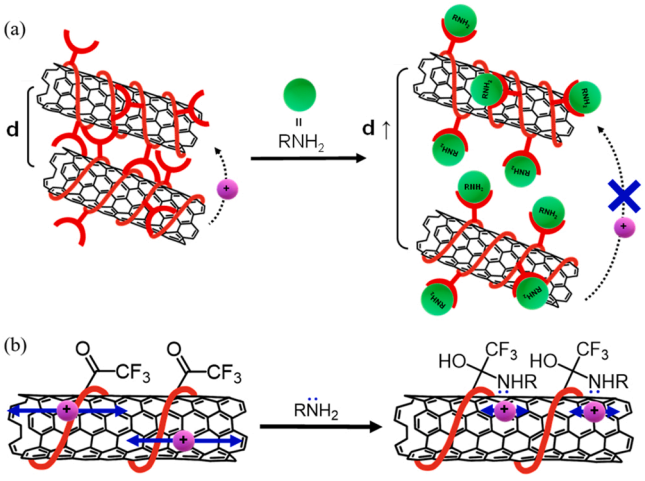

Fig. 7. Schemes of sensitivity improvements in TFMK-P3HT/CNT. (a) The inter-CNT effect, wherein amines could be efficiently captured and thus increase inter-CNT distances, reducing the carrier tunneling. (b) The intra-CNT effect, wherein lone-pair electrons in amines could trap the holes in CNT, lowering the hole mobility.

Methodology, Investigation. **Haneul Kim**: Methodology, Investigation. **Eun Hye Lee**: Methodology, Investigation. **Dong Hyun Lee**: Supervision. **Jong H. Kim**: Conceptualization, Supervision. **Byungjin Koo**: Conceptualization, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.snb.2022.132076.

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