# Selective and Sensitive TNT Sensors Using Biomimetic Polydiacetylene-Coated CNT-FETs

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Miniaturized smart sensors that can perform sensitive, selective, and real-time detection of explosive molecules are crucial for our security as well as the environment and human health. 2,4,6-Trinitrotoluene (TNT) is one of the best-known explosives, but it is also recognized as an environmental pollutant distributed in air, water, and soil. Due to its toxicity, TNT exposure can result in severe adverse effects on human health, particularly targeting the circulatory system, liver, spleen, and immune system.[1] Moreover, TNT and its biodegradation products are mutagenic, carcinogenic, and otherwise harmful to aquatic and terrestrial life.[2,3] Accordingly, the U.S. Environmental Protection Agency has set the maximum allowable limit of 2 ppb for TNT in drinking water.[4] To detect TNT and its metabolites, many laboratory techniques, such as high-performance liquid chromatography (HPLC)-UV, gas chromatography–mass spectrometry (GC-MS), surface-enhanced Raman spectroscopy (SERS), nuclear quadrupole resonance, ion mobility spectrometry, and various other spectroscopic methods are available.[5,6] However, they require expensive and sophisticated instrumentation or complicated sample preparation processes. Recent advances in nano- and biotechnology have led to great progress in the detection of TNT.[7−18] These examples include a semiconducting organic polymer-based laser device,[12] silicon nanowire sensor arrays modified with an amine-functionalized silane derivative layer,[13] and a dual nanosensor based on the electrochemical reduction of TNT and the interaction of the reduction products with conducti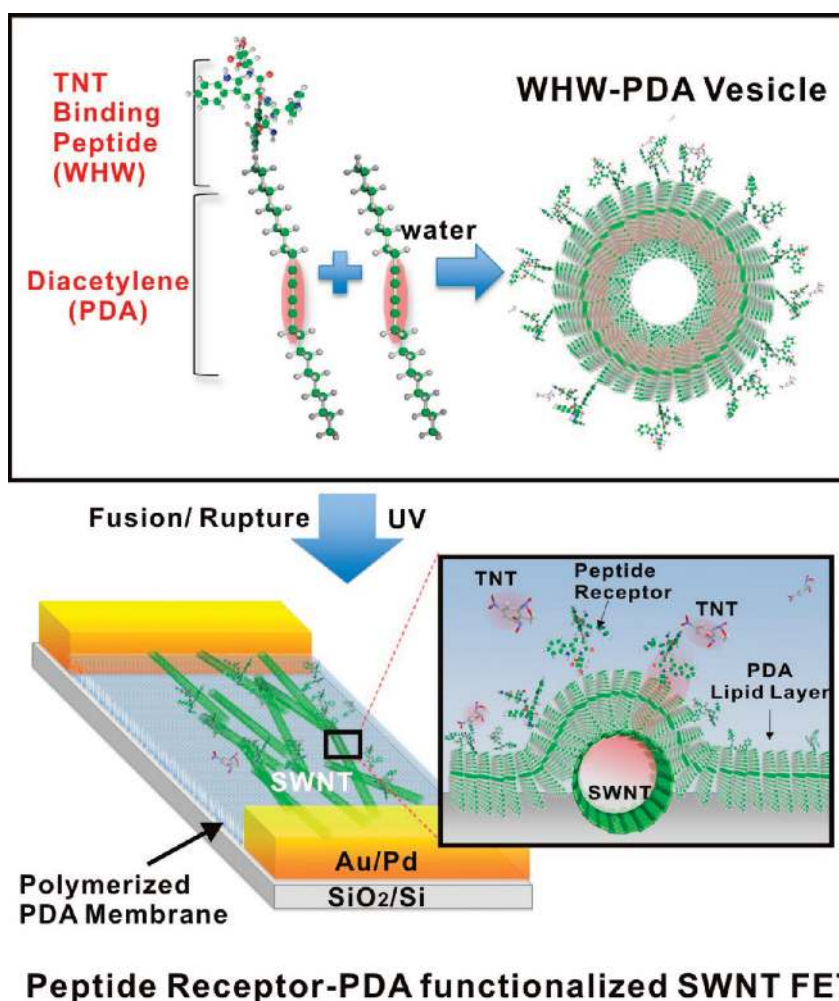ng polymer nanojunctions.[14] These approaches based on nano- and biotechnology are highly efficient and in many cases are remarkably sensitive, with detection limits down to the picomolar range, providing a significant contribution to assays for TNT. However, sensitive microelectronic devices in general suffer from false positive responses against interfering analytes or molecules with similar chemical structures, while most bioassays require multiple sample-processing steps resulting in long response times. Therefore, current sensing technologies for TNT molecules are still far from fulfilling the requirements of selectivity, sensitivity, and real-time detection. Improvements are needed to develop a technology which effectively combines the sensitivity, portability, and real-time detection of microelectronic devices with the selectivity and reliability of biological recognition. Here, we describe a novel, selective, and sensitive nanocoating material consisting of TNT receptors linked to a conjugated polymer, polydiacetylene (PDA), for the

**ABSTRACT** Miniaturized smart sensors that can perform sensitive and selective real-time monitoring of target analytes are tremendously valuable for various sensing applications. We developed selective nanocoatings by combining trinitrotoluene (TNT) receptors bound to conjugated polydiacetylene (PDA) polymers with single-walled carbon nanotube field-effect transistors (SWNT-FET). Selective binding events between the TNT molecules and phage display derived TNT receptors were effectively transduced to sensitive SWNT-FET conductance sensors through the PDA coating layers. The resulting sensors exhibited an unprecedented 1 fM sensitivity toward TNT in real time, with excellent selectivity over various similar aromatic compounds. Our biomimetic receptor coating approach may be useful for the development of sensitive and selective micro- and nanoelectronic sensor devices for various other target analytes.

**KEYWORDS:** lipid membrane receptor · polydiacetylene · trinitrotoluene · carbon nanotube · TNT sensor

**Figure 1.** Schematic diagram depicting our TNT sensors based on WHW-PDA (TNT-binding peptide conjugated with polydiacetylene polymer) functionalized SWNT-FETs. After formation of WHW-PDA/PDA vesicles in $H_2O$, we applied the vesicles to a SWNT-FET, which resulted in rupture, fusion, and UV polymerization of the WHW-PDA/PDA membranes on the SWNT-FET. The molecules and SWNT are not drawn to scale.

functionalization of SWNT field-effect transistors (FET) (Figure 1). The tripeptide TNT receptor (tryptophan-histidine-tryptophan: WHW) was discovered through phage display.[19] The newly developed PDA-TNT receptor coating material efficiently transduced selective binding events between WHW receptor and TNT to the sensitive SWNT-FET conductance sensors. The resulting sensors reproducibly exhibited excellent selectivity with 1 fM sensitivity in real-time. The device's selectivity was demonstrated against other molecules having chemical structures similar to TNT [*e.g.*, DNT (dinitrotoluene), 2NT (2-nitrotoluene), and 4NT (4-nitrotoluene)]. We believe that our selective receptor development method using a rapid evolutionary screening process and subsequent receptor conjugation with a sensitive transducing PDA layer can be generalized to create many other sensitive and selective coating materials. This offers the potential for sensitive microelectronic sensor devices to be created for other target small molecules of interest.

## RESULTS AND DISCUSSION

PDA is a lipid-like polymer composed of a conjugated polymer backbone with carboxylic acid and alkyl side chains. The amphiphilic nature of PDA monomers facilitates its formation into supramolecular assemblies such as vesicles and membranes.[20−22] PDA's conjugated polymer backbone can serve as a stable and sensitive colorimetric sensor due to changes in its conjugated electronic band structure resulting from interactions between target analytes and specific functional motifs on PDA's head groups.[23−26] Therefore, by conjugating PDA with TNT receptor motifs, we can interface selective biological recognition elements with sensitive electronic sensor devices for the purpose of TNT detection. The recognition motif with selective binding capabilities for TNT had previously been identified by our group through the directed evolutionary screening process of phage display against TNT.[19] Using various mass sensing platforms, we demonstrated that the identified

peptides exhibited remarkable selectivity between TNT and DNT explosives in liquid and gas phases after chemical conjugation with poly(ethylene-co-glycidyl methacrylate) or polyethylene glycol.[19,27] Furthermore, we recently synthesized PDA polymers conjugated with TNT receptors (WHW peptide motif) through FMOC solid-phase peptide synthesis approach[28] and demonstrated that TNT-receptor-coupled PDA could form nanometer-sized vesicles (average diameter of ∼150 nm). The resulting nanovesicles possessing the diacetylene $\pi$-electron-conjugated backbones could transduce the binding activity of the TNT target molecules by exhibiting specific color changes upon exposure to the TNT molecules.[29] Therefore, these electronic band structure changes on the PDA polymer backbone might be detected by coupling the electronic structure change to other electronic sensors such as CNT-FETs.

First, we verified that PDA layers can be used as a nanoscale coating material for CNT-FETs. We fabricated a PDA-coated SWNT-FET by expanding the methods reported previously (detailed methods can be found in the Materials and Methods).[30−32] In addition, we characterized their device performances (Figure S1 in Supporting Information) and the uniformity of fabrication (Figure S2; a detailed discussion is in the Supporting Information). Here, the CNT channel consisted of a network of single and bundled CNTs, which resulted in a combination of semiconducting and metallic paths. Only the semiconducting paths in the network contributed to the current change from external stimuli, while the metallic and bundled CNTs formed metallic paths which were not modulated by external stimuli. The SWNT-FETs were then coated with a PDA-conjugated lipid membrane structure *via* vesicle rupture and fusion,[33] followed by UV polymerization (Figure 1). Figure 2A,C shows the optical and AFM topographic images of a SWNT-FET sensor platform, respectively, before the lipid membrane coating. In order to optimize the coverage of our nanocoating materials on SWNT-FETs, we applied the coatings at concentrations ranging from 10 $\mu$M to 10 mM and examined the surface of the modified SWNT-FET by fluorescence microscopy.[25] When 1 $\mu$L of 10 mM WHW-PDA/PDA in deionized (DI) water was applied to SWNT-FET devices, we observed a uniform fluorescence intensity signal over the whole surface, including the octadecyltrichlorosilane (OTS) and SWNT network regions (Figure 2B,D,E). This suggests that the WHW-PDA/PDA-conjugated polymer layers were created evenly on the device surfaces. The conjugated PDA polymer layers were also formed on the SWNT−metal contact region and metal electrodes.

In order to test our hypothesis that sensitive CNT-FETs can detect the electronic band structure changes on the diacetylene $\pi$-electron-conjugated backbones, we investigated the effects of conformational changes incurred by heat treatment on the electric properties of SWNT-FETs. PDA-coated SWNT-FETs were heated with
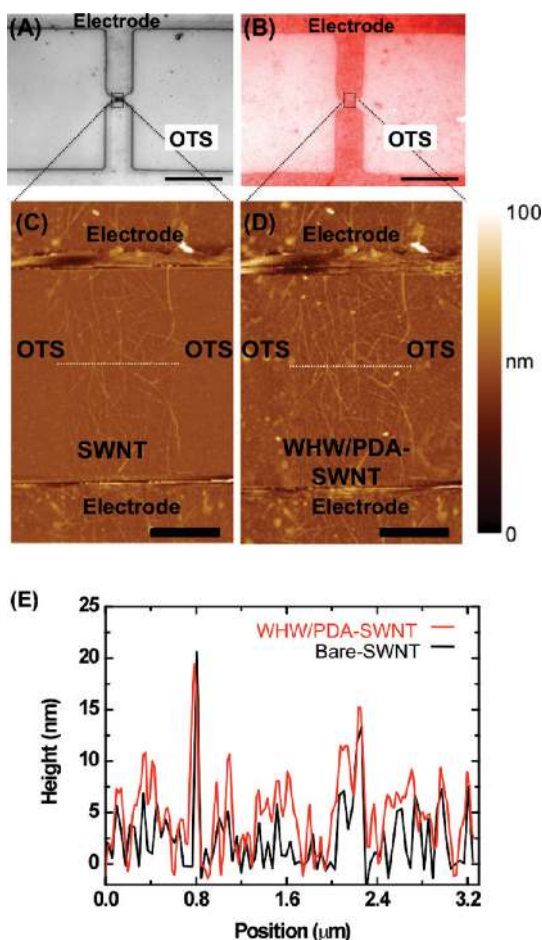


Figure 2. Structure of TNT sensors based on PDA-functionalized SWNT-FETs. (A) Monochromic optical microscopy image of SWNT-FET devices. (B) Fluorescence microscopy images overlaid with optical images of the SWNT-FET after deposition of PDA nanocoating materials on the top of SWNT-FET. (C) AFM images of SWNT-FET before and (D) after the deposition of WHW/PDA coating materials. (E) Height profiles of the cross section (dotted lines in C and D) showed that height increased ∼1.5 nm after deposition of WHW/PDA coating materials. Scale bars are 50 $\mu$m for panels A and B and 2 $\mu$m for C and D.

stepwise temperature increases from room temperature (25 °C) to 80 °C (Figure S3) to induce conformational changes in the PDA backbone while monitoring their conductance. In addition, using a fiber-optic UV/vis spectrophotometer (USB2000, Ocean Optics, Dunedin, FL), reflectance changes were monitored and correlated to the conformational changes of the conjugated PDA membranes. With stepwise increases of temperature, the films exhibited red-shift thermochromic transition which increased the reflected light intensity in the 550−700 nm region (Figure S3A). With the decrease of the $\pi$-conjugated chain length of the PDA backbones, we could observe the stepwise change in conductance of the PDA-coated SWNT-FET devices (Figure S3B). The bare SWNT-FET also exhibited stepwise increases in conductance, but the changes were much smaller. This shows that the conjugated PDA polymers can efficiently transduce their electronic
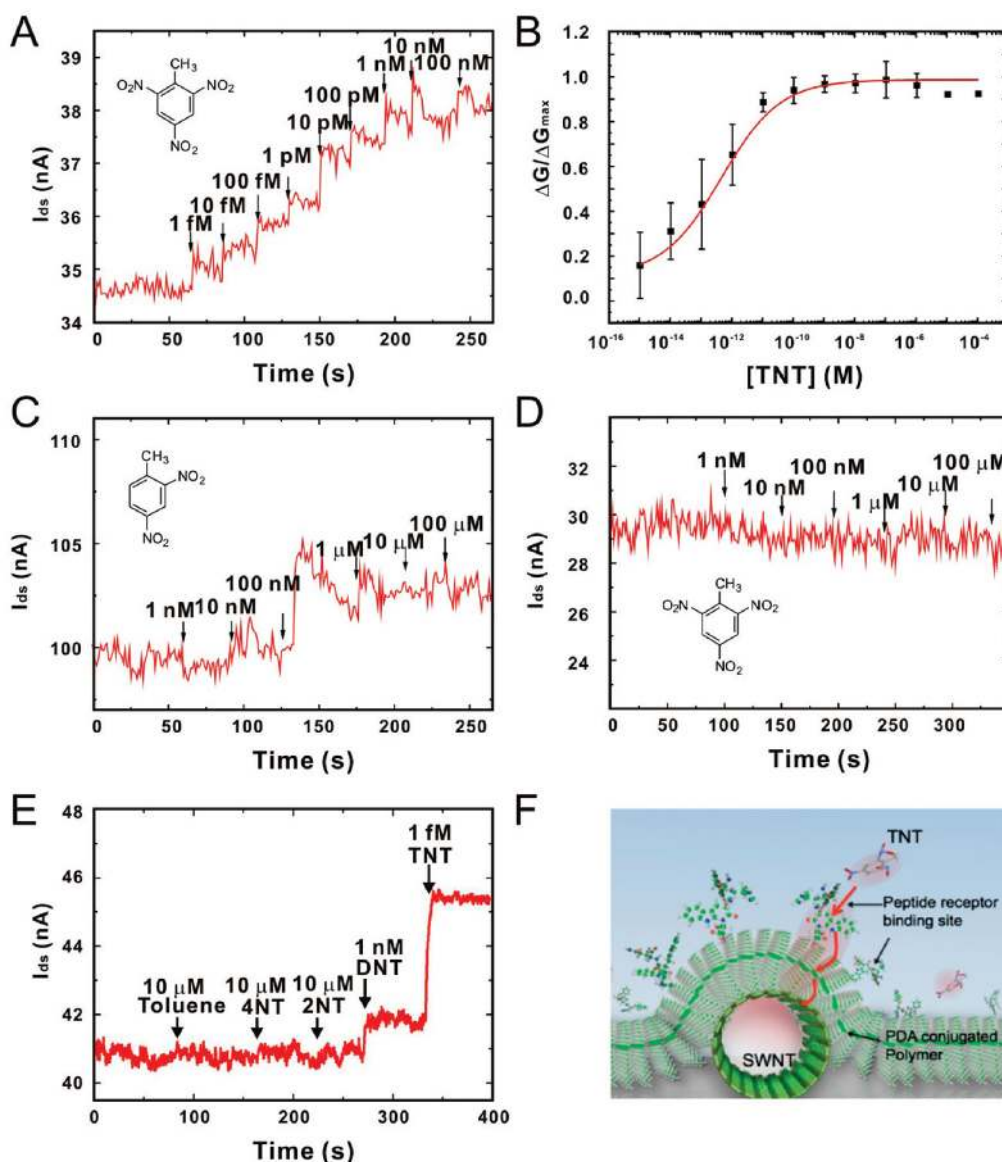
**Figure 3. Specific and sensitive detection of TNT molecules with our TNT sensors based on WHW-PDA-functionalized SWNT-FETs. (A)** Real-time conductance measurements obtained from the WHW-PDA-functionalized SWNT-FETs after the introduction of TNT at various concentrations. Arrows indicate the injection points of target molecules. **(B)** Calibration curve for TNT real-time conductance measurements obtained from the WHW-PDA-functionalized SWNT-FETs after the introduction of TNT at various concentrations. **(C)** Representative conductance measurements of WHW-PDA-functionalized SWNT-FETs to DNT. **(D)** Response of PDA-functionalized SWNT-FETs without WHW-PDA to TNT. **(E)** Selective response to TNT in mixed solution of toluene, 4NT, 2NT, and DNT. **(F)** Possible mechanism of signal transduction of electronic cloud perturbation from the selective molecular recognition peptide to sensitive SWNT-FET.

structure perturbation caused by external stimuli to the SWNT-FET devices.

Afterwards, we incorporated the TNT receptor peptides (WHW) with the PDA transducing material to functionalize the CNT-FETs and observed the selectivity and sensitivity of the CNT-based sensors. Previously, we characterized the optimum density of receptor for signal transduction using UV/vis studies[29] and verified that a 4:96 molar ratio between WHW-PDA and PDA was the most effective. Therefore, we used this molar ratio of WHW-PDA/PDA for coating SWNT-FETs during device fabrication. Electrical sensing of the target TNT and other control chemicals was carried out in real time by monitoring the

source−drain currents of WHW-PDA-functionalized SWNT-FETs in response to the addition of target analytes at a concentration range between 1 fM to 100 $\mu$M in deionized water (DI) (see details in Materials and Methods). The electrical conductance measurement exhibited detectable responses to TNT concentrations of 1 fM to 100 nM (Figure 3A). The electrical conductance of our sensor showed significantly increased sensing response to TNT from 1 fM to 1 nM and then a gradual saturation from 10 nM. We were able to achieve down to 1 fM detection, which shows high sensitivity compared to previous TNT sensors using different transducers.[12,14,17,18] This indicates that, with the addition of TNT, the increase

and gradual saturation in conductance was caused by the binding between the receptor domain of WHW-PDA and TNT, which is in good agreement with our previous results.[19,27] The increased conductance of the sensor can be explained by the chemical gating effects caused by binding of TNT to WHW-PDA/SWNTs with signal amplification through the conjugated PDA, which induced additional positive charges in the SWNTs, thus increasing the conductance of p-type SWNTs.[34] Due to the intrinsic nature of the CNT-FET, we observed a different magnitude of the sensitive response upon the addition of TNT analytes. Therefore, a calibration curve was obtained as a function of TNT concentration using the normalization of conductance, $\Delta G/\Delta G_{max}$, where $\Delta G_{max}$ represents the conductance change at a saturation level of conductance $G$ due to the interaction between TNT and WHW-PDA-modified SWNT-FETs (Figure 3B). The curve for TNT estimations with our sensors exhibited a wide dynamic range (1 fM to 1 nM) over which there were measurable responses and a sensitive linear range with a steep slope of ~0.16/decade. The addition of DNT also caused a conductance increase of WHW-PDA-functionalized SWNT-FETs, however, only at a higher concentration of 100 nM, which is a $10^8$ times higher concentration than the detection limit of TNT (Figure 3C). When we performed the same measurement with the SWNT-FET devices coated with polymerized PDA without WHW receptor motifs, the electrical conductance of the device exhibited almost no change upon the addition of TNT or DNT at a concentration from 1 nM to 100 $\mu$M (Figure 3D and Figure S4 in Supporting Information). This clearly shows that we can effectively passivate the sensitive SWNT-FETs using polymerized PDA lipid layers to prevent nonspecific binding between the SWNT and TNT molecules.

The specificity of our sensor toward interfering molecules was tested by extensive control experiments using various aromatic compounds with similar chemical structures to TNT, including toluene, 2NT, and 4NT. All electrical conductance measurements exhibited almost no change upon the addition of control analytes (Figure S5 in Supporting Information). Only the addition of TNT caused a conductance increase starting from 1 fM concentration, revealing the exceptional selectivity of this sensor (Figure S6). The rapid measurement of a WHW-PDA-functionalized SWNT-FET in a mixed solution of toluene, 4NT, 2NT, DNT, and TNT also confirmed the selective conductance enhancement only by the addition of TNT (Figure 3E). As seen from this control experiment, addition of 10 $\mu$M toluene, 2NT, 4NT, and 1 nM DNT negligibly affected the sensor, while the addition of a 1 fM TNT solution caused a sharp increase in conductance. Although we cannot exclude that our PDA-based nanocoating materials system might exhibit a response to a real-world interferent, this result demonstrates that our system is highly selective to distinguish TNT target analytes over other control molecules with similar chemical structures.

On the basis of our experimental data, we propose the following possible mechanism for efficient signal transduction between the TNT sensing nanocoating materials and sensitive SWNT-FETs depicted in Figure 3F. First, the recognition peptide can selectively distinguish the TNT target *versus* many other similar chemicals through multivalent interactions. During the binding events, we expect that the $\pi$ electrons of the TNT molecule interact with the electron-rich $\pi$ orbital environment of the three aromatic side chains of the WHW peptide (red arrows in Figure 3F). Because the distance between the electron-rich binding site and conjugated PDA is within 1 nm, these binding events can further perturb the conjugated PDA electronic band structure, which causes a chromic shift. Because sensitive SWNT-FETs are within the vicinity of ~1.5 nm from the PDA-conjugated backbone, these electronic perturbation can be detected through electric conductance signals in a sensitive and selective manner.

## CONCLUSION

We have developed a rapid and selective TNT sensor with 1 fM sensitivity through the combination of SWNT-FETs and PDA-based lipid membranes coupled with biologically inspired TNT peptide receptors to significantly improve selectivity in a nanoelectronic device sensor. In our system, a sensitive SWNT-FET interfaced with PDA was exploited to transduce the binding activities between the target TNT and its TNT-selective binding peptide receptor. Conjugated PDA-based lipid-like polymers provided a stable coating platform to interconnect the selective TNT receptor and sensitive FET devices. In order to be a practical, real-world sensor, further improvement in our sensing system is desired. First of all, reversibility of the sensor may allow for detection of changes in the amount of analyte present. Second, the entire sensing system should be packagable into a small portable electronic device. Finally, it would be favorable to have multiplexed detection of other important explosives, including RDX (1,3,5-trinitroperhydro-1,3,5-triazine), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), and PETN (pentaerythritol tetranitrate), with parts per trillion sensitivity due to the low vapor pressure of these explosive molecules (~$10^{-9}$ Torr). Our modular approach (to develop selective receptors through evolutionary processes, to conjugate the receptors with effective transducing lipid coating layer, and to fabricate selective and efficient coating layers onto sensitive microelectronic devices) could provide a powerful system for the further development of selective, sensitive, and real-time sensors for various other small molecules, including poisonous volatile organics, pesticides/insecticides, biotoxins, and pathogens. The

success of the advanced architecture of the polymerized lipid/nanoelectronic hybrid device could also provide strong support for biological/chemical sensing, diagnostics, and drug screening.

## MATERIALS AND METHODS

**SWNT-FET Fabrication.** Octadecyltrichlorosilane (OTS) self-assembled monolayer (SAM) with nonpolar terminal groups was patterned on a $SiO_2$ surface using photolithography. When the patterned substrate was placed in the solution of SWNTs (0.1 mg/mL in o-dichlorobenzene), a single layer of SWNTs was selectively adsorbed onto bare $SiO_2$ regions. Afterward, electrodes (30 nm Au on 10 nm Pd) were fabricated using conventional photolithography.

**PDA—Peptide Conjugate Synthesis.** To produce PDA—peptide conjugates, standard solid-phase peptide synthesis was carried out using FMOC chemistry.[28] Resins were preswelled for 30 min in NMP prior to deprotection. Deprotection steps using 3 mL of 3% DBU in NMP were carried out for 20 min on a rocking platform. The washing steps proceeded as follows: 3 washes with 4 mL of NMP, 6 washes with the series of 4 mL of methanol followed by 4 mL of dichloromethane, and 3 washes with 4 mL of NMP. Coupling steps of 3 mL and 0.2 M amino acid, Hobt, and DIC were carried out on a rocking platform for 2 h. A final coupling step with 3 mL of 0.2 M PDA, Hobt, and DIC was performed with the same incubation period of 2 h to create the PDA—peptide conjugate. Resins were washed with methylene chloride, dried, and underwent cleavage. Cleavage reactions were performed for 2 h while shaking with a cocktail of 82.5% trifluoroacetic acid, 5% water, 5% phenol, 5% ethanedithiol, and 2.5% triisopropylsilane. Rotary evaporation followed by precipitation in diethyl ether provided the removal of cleavage solvents and protecting groups. Samples were then suspended and mixed in water followed by centrifugation for 10 min at 10 000 rpm to pellet the product at which point the supernatant was discarded to remove any trace contaminants. The suspension and centrifugation steps were repeated until all cleavage contaminants were removed. Lyophilization was then performed, and samples were stored at 4 °C. The PDA—peptide conjugates that were synthesized are as follows: W-PDA (promoter) and WHW-PDA (TNT binding motif). Molecular weight of the synthesized peptide was confirmed using liquid chromatography mass spectrometry (LC-MS) before constructing the target vesicles (data not shown).

**Controlling Surface Composition and Density in Supramolecular Assemblies.** PDA and WHW-PDA were suspended to 10 mM in water. Solutions were sonicated for 20 min and heated at 85 °C for 20 min to melt any existing supermolecular structure. Additional sonication for 20 min was performed prior to mixing of PDA with peptide—PDA conjugates. Volumetric mixing was utilized to provide the exact molar amount of PDA and peptide conjugate. After mixing, the sample was heated for another 5 min at 85 °C and sonicated to ensure ample distribution of PDA—peptide conjugates and PDA. To allow self-assembly into vesicle structures, the solution was allowed to cool to room temperature then incubated at 4 °C for 24 h. The solution was then brought to room temperature. When vesicles were incubated on the SWNT-FET surface, a lipid layer formed spontaneously via vesicle rupture and fusion. Polymerization was carried out for 25 min of exposure using a 4 W UV lamp at 254 nm wavelength.

**Characterization of TNT Sensing Using SWNT-FETs.** The electrical sensing characterization of the target TNT and other control chemicals was carried out in real time by monitoring the source—drain currents of WHW-PDA-functionalized SWNT-FETs in response to the addition of target analytes at a concentration range between 1 fM and 100 $\mu$M in deionized water (DI). We used an HP 4155A semiconductor parameter analyzer (Agilent Technologies, Santa Clara, CA). Before reaction, droplets of DI water were placed on the SWNT-FET. Here, 0.01 V was applied between the source—drain electrodes, while the platinum liquid gate was grounded. Then, the solution of a specific target was added, resulting in a given concentration, while monitoring the change of current levels using a semiconductor parameter analyzer.

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