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Mingling Electronic Chemical Sensors with Supramolecular Host-Guest Chemistry

Congzhi Zhu and Lei Fang*

Department of Chemistry, Texas A&M University, 3255 TAMU, College Station, TX 77843, USA

Abstract: Supramolecular host-guest chemistry allows sensitive and selective recognition of a certain substrate by using a rationally designed receptor. Such a molecular receptor can be incorporated into an electronic chemical sensor so that the anticipated host-guest binding event can be transduced directly into electric signals. In particular, chemiresistors and chemically sensitive field-effect transistors report the change of conductance/resistance of the active conducting materials upon the desired supramolecular binding event *via* varied mechanisms. This mini-review highlights the recent advances in the development of electronic sensors, in which the active conducting/semiconducting materials are incorporated with specific supramolecular receptors. Depending on the nature of the active conducting layer, these devices can be categorized into carbon materials-based sensors and organic semiconductor-based sensors. At the end of this review, an outlook of the related field is provided and discussed.

Keywords: Carbon nanotubes, chemiresistor, electronic sensor, field-effect transistor, host-guest interaction, molecular recognition, organic semiconductor, supramolecular chemistry.

1. INTRODUCTION

Supramolecular chemistry encompasses the subdisciplines involving non-covalent intermolecular interactions [1, 2]. Molecular recognition, depending on the so-called “host-guest” [3] principle, is one of the cornerstone of supramolecular chemistry [4, 5]. By rational design, synthetic chemists are able to construct receptors (host) that complement the desired substrate (guest) in shape (geometry) and binding affinities (energy) [6] leading to highly sensitive and selective interactions between the receptor and the substrate. Consequently, the development of molecular sensors for differential sensing became one of the most promising applications of such host-guest recognition [4, 5]. Chemists have successfully designed and constructed receptors possessing shapes, dimensions, and complementary binding affinities suitable for hosting various substrates, including cations [7], anions [8], radicals [9] and neutral small molecules [10]. The sophisticated molecular design allows highly selective host-guest interactions with sufficient free energy stabilization through preorganized formation of H-bonds [11], π-π stacking [12], hydrophobic interactions [13], or electrostatic forces [14], *etc.* In a sensing system, depending on the dynamic exchange of the non-covalent bonds between the hosts and the guests, the binding events result in macroscopic signal modulations upon the addition of the target analyte. In other words, a supramolecular sensor combines highly selective and sensitive host-guest recognition with a certain form of reporter, so the presence of the guest can be detected [15]. These features grant supramolecular sensors a bright future in the applications of bioanalysis, celluar imaging, environmental analysis, and quality control [15].

In the past few decades, numerous supramolecular sensors that transduce the non-covalent host-guest interactions into varied responding signals have been developed [16]. Since the dawn of host-guest chemistry, it has been an intriguing research subject to directly transduce supramolecular binding events into electric signals, such as changes in resistance, potential, current density or capacitance. The development of electronic chemical sensors, indeed, thrived as a result of multi-disciplinary amalgamation of organic chemistry, physical chemistry, analytical chemistry, materials science, and electrical engineering. In general, based on their device architectures, electronic chemical sensors can be divided into the following categories: chemically sensitive field-effect transistors (CHEMFET) [10,17], ion selective electrodes (ISE) [18] and ion selective field effect transistors (ISFET) [19], chemiresistors [20], as well as chemicapacitors [21]. The incorporation of host-guest interactions into these electronic sensors imparted superior selectivity and sensitivity into the course of differential sensing.

The focus of this mini-review is to highlight the recent advances in the development of electronic sensors that are incorporated with specific supramolecular receptors in the *active conducting/semiconducting layer*. Although the device architecture could

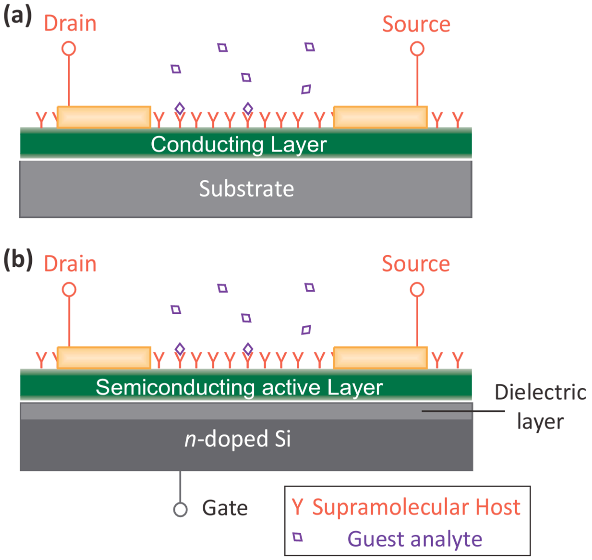

Fig. (1). Graphical representation of the device architectures of (**a**) an FET chemical sensor and (**b**) a chemiresistor.

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*Address correspondence to this author at the Department of Chemistry, Texas A&M University, 3255 TAMU, College Station, TX 77843, USA; Tel: +1-979-845-3186; Fax: +1-979-845-4719; E-mail: fang@chem.tamu.edu

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be in the forms of field-effect resistor (FET) or simple resistor, the principal mechanisms of the detection are similar: Modulation of the conductivity of the active conducting materials upon the host-guest binding event. In this context, this article is structured based on the nature of the conducting materials, instead of the architecture of the sensor device. The relatively mature field of membrane-based ISE and ISFET are not discussed extensively here, because the employment of supramolecular receptor in these potentiometric sensors for selective detection of cations and anions has already been the subjects of a number of comprehensive review articles [22-25]. Furthermore, this review does not discuss electronic chemical sensors that rely on simple chemical binding events without specific host-guest interactions. Readers interested in those general electronic sensors could find the corresponding comprehensive review articles [26-28] in the literature as well.

2. MECHANISM AND DEVICE ARCHITECTURE

In a supramolecular electronic sensor, the detection takes place through two steps, namely, molecular recognition and signal transduction [5]. In the first step, the key challenges are the sensitivity and selectivity of the host-guest interaction. In order to achieve a high *sensitivity*, the supramolecular binding affinity between the receptor (host) and the substrate (guest) needs to be as high as possible. Thus, the receptor and its substrates should be in contact over a large area; meanwhile, this contact can induce a big free energy release. In other words, ideal artificial receptors must contain cavities sufficiently large to allow substrate inclusion and multivalent non-covalent interactions [6]. On the other hand, a good *selectivity* comes from designed geometric and dynamic features of the receptor that is complementary exclusively to the desired analyte, but not to other possible interfering substrates [5]. As a result, a macropolycyclic architecture with a relatively rigid backbone [29] is often the *de-facto* choice. Indeed, the most prominent selective receptors are those with these structural features, such as cyclodextrins [30], cucurbiturils [31], pillarenes [32-34], calixarenes [35], and cyclobisparaquats [36], *etc*. It is worthy to mention that biological receptors that possess these features can also be considered as supramolecular hosts with excellent molecular recognition abilities. Several examples with biological receptors are discussed in this article as well.

The signal transduction is another crucial step in determining the sensitivity. In electronic sensors, the binding events are usually transduced into modulations in current/resistance, potential, capacitance, or impedance. Herein, we focus primarily on the sensors with current or resistance change, mainly including chemiresistors and CHEMFET. The key component of a chemiresistors device is a chemically sensitive conductive film that is deposited between two electrodes (Fig. **1a**). Upon application of a potential, there is a measurable current or resistance across the film. When the thin film interacts to a chemical analyte of interest, the conductive film could exhibit a change in resistance/conductance as the readout [28]. There are a variety of different mechanisms that could lead to such a change, including doping, swelling, conformational change, charge carrier density change, introduction of traps, and charge transfer, *etc*. In general, chemiresistive sensors possess the advantages of feasible fabrication and minimal power requirement.

A CHEMFET sensor, on the other hand, consists of a semiconducting film deposited between two metal electrodes (drain and source) and a gate electrode that modulates the on/off of the drain-source current (Fig. **1b**). The chemical detection could be achieved by altering either the gate-generated electrostatic field or the charge transport rate of the semiconducting film. The former mechanism has been employed in many ISFET [23, 27], which is not the main focus of this mini-review. The latter mechanism, however, resembles that of a simple chemiresistors, as the readout of the sensor device depends on the conductivity/resistance of the active thin film. Compared to chemiresistors, CHEMFET sensors offer the additional advantages of multi-parameter readout and signal ampli-

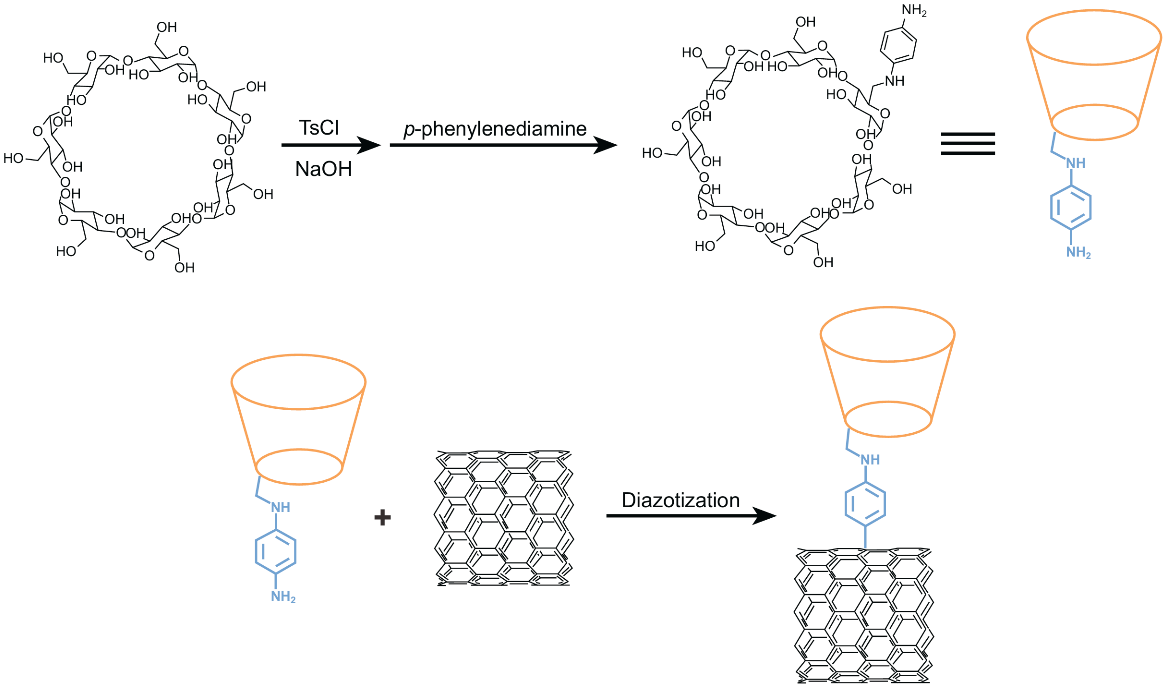

Fig. (2). The synthesis of PCD from *β*-cyclodextrin and its covalent attachment onto SWCNTs. (Ref. 43).

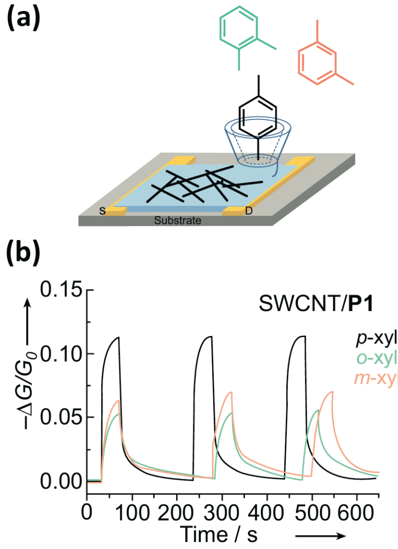

Fig. (3). **a**) Schematic view of the selective binding with *p*-xylene through the modification of *p-tert*-butylcalix[4]arene-substituted polythiophene on a SWCNT-based device. **b**) Conductance change $\Delta G/G_0$ of the chemiresistor as it responses to xylene isomers. [Adapted with permission from reference 20].

fication [37-39]. Traditionally, they have been used for vapor-phase detection through a serendipitously discovered sensitivity of the semiconductor materials to a number of chemical species, such as alcohols, alkenes, esters and lactic acids [40]. Nowadays, chemical modification on the semiconducting layer allows a sensitive and selective detection for a boarder range of analytes [10, 41].

3. SENSORS BASED ON CARBON ACTIVE MATERIALS

Carbon nanotubes (CNTs) are leading candidates as chemiresistor and CHEMFET materials because of their superior mechanical and electrical properties [42]. A strong charge transfer interaction that leads to a change in conductance contributes to a high sensitivity of CNT chemiresistor sensors, especially those based on single-walled carbon nanotubes (SWCNTs). However, this type of charge transfer interaction only allows the detection of aromatic molecules, thereby the analyte scope is limited. In addition, undecorated SWCNTs show poor selectivity towards different substrates. The incorporation of host-guest recognition sites on CNTs, in this context, has been an effective strategy to address these issues.

An example of such incorporation can be represented by the covalent attachment of cyclodextrin derivatives onto SWCNTs. Mono-6-deoxy-6-(*p*-aminophenylamino)-*β*-cyclodextrin (PCD), a selective host for persistent organic pollutants (POPs), was covalently deposited onto SWCNTs (Fig. **2**) [43]. A highly sensitive detection of POPs, such as 2,4,5-trichlorobiphenyl (TCB), was achieved through the host-guest interaction between the hydrophobic cavity inside PCD and the POP molecules. Following the functionalization with PCD through diazotization, SWCNTs were spin-coated onto a SiO_2/Si substrate that was pre-deposited with electrodes, consequently affording a chemiresistor device. Because the capture of POPs could result in the charge redistribution of cyclodextrin, an induced charge transfer from PCD subsequently decreased the charge carrier density in SWCNTs. As a result, after being exposed to POP molecules, the hybrid nanotubes saw a decrease in the conductance. The ratio of such change was used as a readout signal, which was correlated on the concentration of POP molecules. This SWCNTs-PCD system held an important potential application on monitoring pollutants in a real-time manner and extended the detection limit to a nanomolar scale.

Covalent modification could potentially damage physical properties of CNTs [44]; therefore, non-covalent attachment, such as *π*-*π* stacking and polymer coating, was more favorable in the development of CNTs-based chemiresistor. Swager *et al*. developed [20] a chemiresistor based on SWCNT/calixarene substituted polythiophene, by taking the advantages of a selective and highly favored host-guest interaction between calixarene with *p*-xylene (Fig. **3a**). Polythiophene moiety was employed as the anchoring point for the non-covalent attachment of calixarene units onto carbon nanotubes through *π*-*π* stacking interaction. This sensor showed high selectivity among regioisomers of xylene with only minor structural differences (*p*-xylene *vs o*- and *m*-xylenes). Carried by airflow, 400 ppm dose of *p*-xylene induced a 12% decrease of conductance on the chemiresistor device. With the same concentration of *o*-xylene or *m*-xylene, however, the decrease of the conductivity was 6% and 7%, respectively. Moreover, the device gave a fast response rate within two minutes (Fig. **3b**). It was speculated that the conductance decrease was a result of reduction in SWCNT-SWCNT interaction by xylene adsorption, corroborated by Raman spectra.

The groups of Stoddart and Grüner used pyrenecyclodextrin-decorated SWCNTs to fabricate FET sensor devices, which were able to detect hydrophobic organic molecules in a selective manner in an aqueous solution [10]. In such SWCNT-based FET devices (Fig. **4a**), the host receptor — a pyrenecyclodextrin derivative, was adsorbed non-covalently onto the surface of SWCNTs. Upon exposure, the organic analyte could be captured in the cavity of the pyrenecyclodextrin derivative on account of hydrophobic interactions. In the presence of certain organic molecules, such as adamantanol and adamantanecarboxylic acid, the threshold voltage of the device shifted to more negative values; hence the source-drain current decreased. Larger molecules such as sodium cholate, however, exerted only marginal change in the V_t and I_{DS}, because the oversized cholate could not fit in the cavity of cyclodextrin. The electrical conductance of the device was highly sensitive to the presence of the guest molecules such as adamantanols and varied significantly with the changes in the binding affinities (Fig. **4b**). In fact, the magnitude of the transistor characteristic movements in the

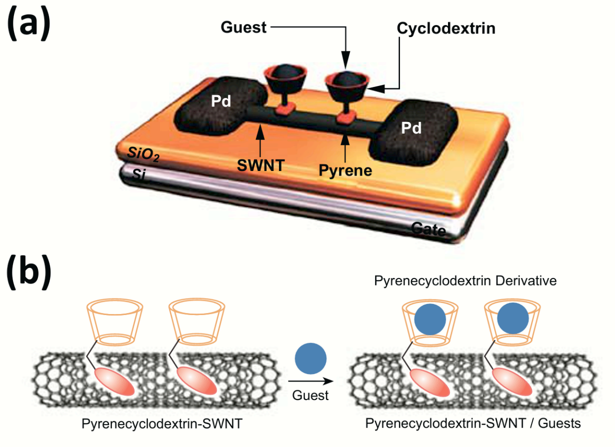

Fig. (4). **a**) Schematic view of the pyrenecyclodextrin-decorated SWCNT and b) the sensing process based on host-guest interaction. [Adapted with permission from reference 10].

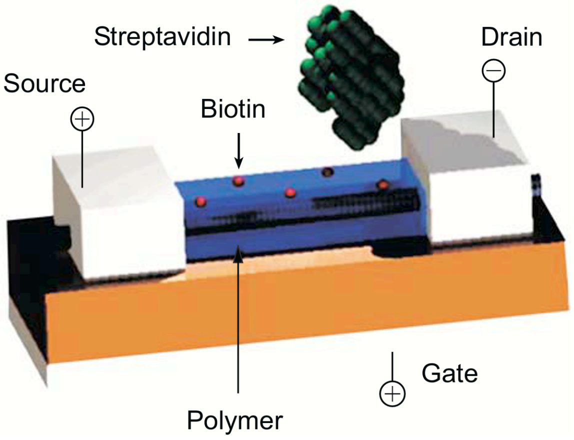

Fig. (5). Schematic view of the polymer-coated SWCNT device decorated with biotins as the supramolecular binding sites. [Adapted with permission from reference 44].

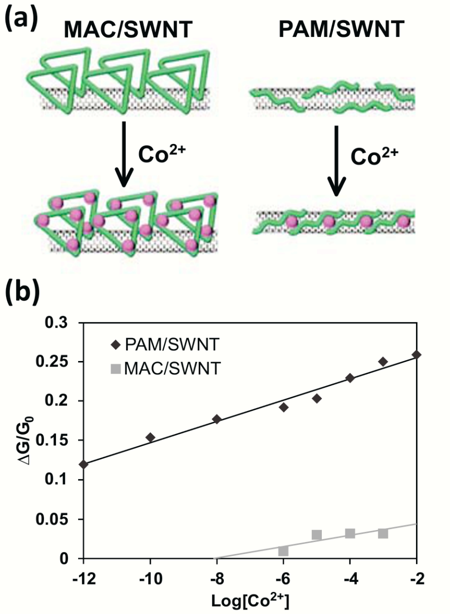

Fig. (6). **a**) Schematic view of the detection of Co^{2+} based on MAC- and PAM-decorated SWCNTs. b) The plot representing a logarithmic relation between the conductance change ratio and the Co^{2+} concentration. [Adapted with permission from reference 45].

presence of the guest molecules depended linearly upon the magnitudes of the supramolecular complex formation constants exhibited by the cyclodextrin with these molecules.

Employing a polymer-coating strategy, Star *et al.* fabricated biotin-decorated CNTs as the semiconducting channel in a FET device and detected the highly specific biotin-streptavidin binding event [44]. The dependence of I_{DS} on the gate voltage was measured as the device characteristic to display the impacts from polymer coating, the attachment of biotins and the binding event (Fig. **5**). Submerging the device in a mixed solution of poly(ethylene imine) (PEI) and poly(ethylene glycol) (PEG) coated the SWCNTs, leading to a device-characteristic shift from the *p*-type conductance to *n*-type conductance. The subsequent covalent modification of biotins enabled a partial recovery of the *p*-type conductance, because the electron density of the primary amino groups on PEI decreased after reacting with biotin-*N*-hydroxyl-succinimide ester. To detect that biotin-streptavidin binding event, this sensor device was exposed to a streptavidin solution under negative gate voltage. Consequently, a notable decrease of I_{DS} was observed and was attributed to the localization of positive ionic entities or the delocalization of negative ionic entities on CNTs. Thus, it was concluded that the decreased I_{DS} was originated from the conformational change of the biotin-streptavidin complex upon binding.

On the basis of metal-ligand coordination–another type of supramolecular interaction, the detection of Co^{2+} was achieved by attaching chelating molecules and polymers onto SWCNTs [45] (Fig. **6a**). Based on the structure of salophen macrocycle (MAC) and its well-known chelating property with metal ions, the Star group synthesized polyazomethine (PAM) containing a similar coordinating moiety as the repeating unit. The hydrophobicity of MAC and PAM allowed their non-covalent attachment to SWCNTs through π-π stacking. The measurement of the conductance of PAM/SWCNT showed an impact from Co^{2+}: a higher Co^{2+} concentration lead to a lower conductance. To compare PAM and MAC on their sensing abilities, a similar detection was carried on with MAC/SWCNT, which gave out a relatively weaker conductance decrease at the same concentration of Co^{2+}. (Fig. **6b**) This difference was attributed to the signal amplification resulted from the rearrangement of PAM upon the addition of Co^{2+}, corroborated by the UV-vis-IR spectra and cyclic voltammetry experiments.

4. SENSORS BASED ON ORGANIC SEMICONDUCTORS

Organic field-effect transistors (OFETs) are leading a position on the development of chemical sensors because of their portability and tenability [46]. OFET sensors were firstly developed as gas sensors as early as in 2000, because a modulation on the current can be observed when the organic semiconductor layer is exposed to analytes [37]. The real-life application of these OFET sensors, however, was limited by their unstability in aqueous conditions and high operation voltages [47]. In addition, despite of an extremely low detection limit, a simple-adsorption-based device suffers from poor selectivity, as a result of the inherent sensitivity of organic semiconductors that often show responses to many chemical species. In order to overcome this challenge, specific supramolecular recognition sites can be incorporated onto the semiconductor layer. Because covalent modifications of the semiconductor layer can lead to an unstable and low-performance device, the non-covalently modified OFETs predominate so far in this field.

The Bao group developed a top-contact/bottom-gate OFET sensor for organic solvent molecules, through non-covalent deposition of calixarene host molecules onto the surface active semiconducting materials [41]. Calixarene features a strong host-guest interaction with a variety of organic solvent molecules. The size match between the calixarene host and the guest solvent molecules improved the selectivity and sensitivity of the host-guest interaction. 5,5′-bis-(7-dodecyl-9H-fluoren-2-yl)-2,2′-biothiophene (DDFTTF) was selected as the semiconducting layer because of its stability and relatively high mobility [48] (Fig. **7a**). The vacuum-deposited 10 nm of DDFTTF layer was thin enough for an efficient response from the bottom conducting channel to the supramolecular bonding event that took place on the surface top. The calixarene layer was deposited on top of the DDFTTF semiconductor layer to give a uniform coverage (Fig. **7b**). The deposition of the calixarene layer did not impact the device characteristics, such as the threshold voltage, average mobility and on/off ratios. Subsequently, in order to evaluate the sensing performance, the OFET sensor was mounted

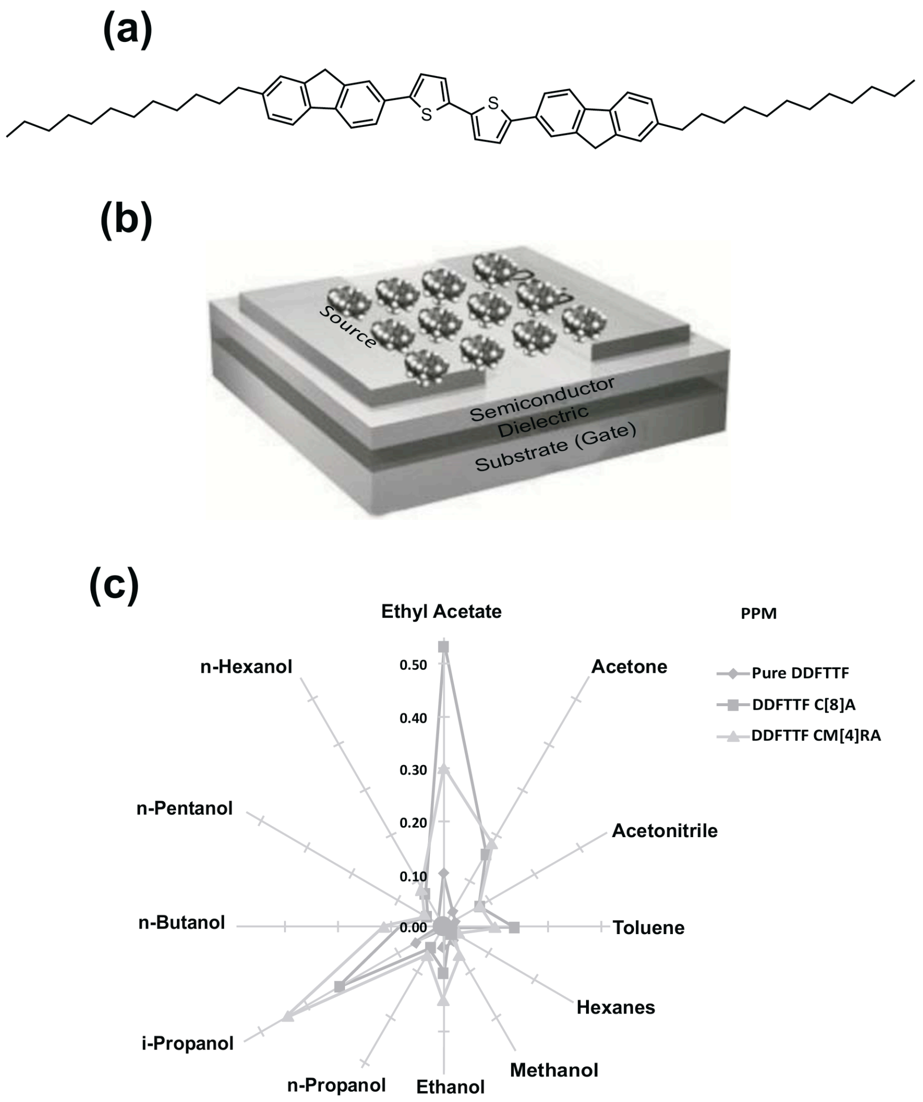

Fig. (7). a) Structural formula of DDFTTF; **b**) Schematic view of the calixarene-fabricated OFET sensor; **c**) Graphical comparisons on the sensing results based on bare OFETs and modified OFETs. [Adapted with permission from reference 41].

beneath an acrylic flow cell, while the source/drain current was monitored versus time. The change in the rate of the drain current was used as the signal readout for the OFET, because it was independent of the gate-bias stress. Contrary to the bare OFET device, the host-guest binding between the calixarene layer and the guest molecules rendered the device a higher rate on current change and an enhanced response to a series of analytes. Both calix[8]arene and *C*-methylcalix[4]resorcinarene were adopted and gave high sensitivities to organic solvent molecules, but they showed disparate selectivities to solvents with assorted sizes on account of the different sizes of their binding cavity. (Fig. **7c**) In addition, the stable nature of calixarene single crystals enabled the device to function well in aqueous conditions [48].

In contrast to the aforementioned method of direct deposition, metal nanoparticles were employed to serve as a platform for the recognition sites to be anchored onto the organic semiconductor layers [47]. In this method, the binding sites were incorporated onto a top-contact/bottom-gate OFET closer to the active layer, compared to the traditional methods that involve the introduction of an insulating polymer onto the semiconductor to accommodate the recognition sites [49]. Such a nanoparticle platform resulted in an increased sensitivity. As a water-stable and high-mobility material, DDFTTF was again employed as the active semiconductor in this work; while an ultrathin layer of poly(4-vinylphenol) and 4,4′-(hexafluoroisopropylidene)dipthalic anhydride was used as the dielectric layer. An ordered array of gold nanoparticles was deposited through spin coating of poly(styrene-*b*-4-vinylpryidine) [50] containing $HAuCl_4$ in its pyridine-core micelles followed by an exposure to oxygen plasma, which removed the polymer and lead to the formation of the nanoparticle array. Subsequently, gold nanoparticles were functionalized independently with a thiolated DNA oligomer that contained a perfectly size-matched host space for Hg^{2+} guest formed by thymine-thymine base mispairing (Fig. **8a**) [51]. Because the introduction of Hg^{2+} induced a conformational change of this oligonucleotide, the resulting higher negative charge density on the DDFTTF surface lead to positive charges formed in the semiconductor, which changed the drain-source current (I_{DS}) correspondingly [52, 53]. Upon the addition of Hg^{2+}, an

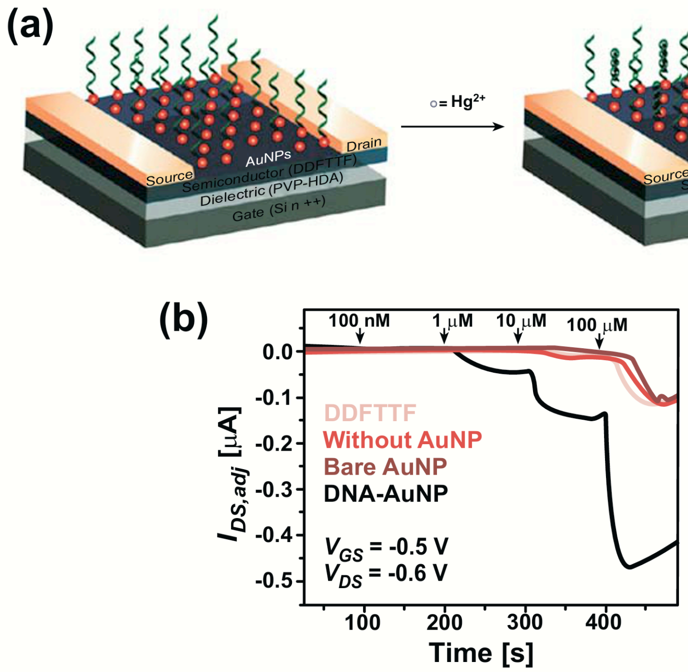

Fig. (8). a) Schematic view of the detection process based on the AuNPs-fabricated OFET sensor. **b**) The graph presenting the results of control experiments and showing the dramatic current increase upon the addition of Hg^{2+} onto the device surface. [Adapted with permission from reference 47].

obvious increase of I_{DS} was observed when the concentration reached the order of 1 μM (Fig. **8b**). In order to detect the tolerance to other metal ions, this device was subjected to different ion solutions, such as Na^+, Mg^{2+}, Ni^{2+}, Cd^{2+}, *etc*. A slight decrease of I_{DS} was detected and was attributed to the increased ionic conductivity in the solution. Furthermore, no significant impact on the detection of Hg^{2+} was observed when the interfering ions, such as Cd^{2+}, Pb^{2+} and Cu^{2+} were added onto the device with Hg^{2+}. In conclusion, this highly Hg^{2+}-selective DNA oligomer allowed a clear detection with minimum interference from other ions. In a separated recent report, a siloxane-functionalized poly(isoindigo-dithiophene) was employed as the active layer. Through a similar strategy based on host-guest interactions, this FET sensor device demonstrated high stability in the marine environment and sensitive detection of Hg^{2+} [54]. Due to the broad range of the gold-thiol chemistry [55, 56], many recognition sites for different analytes can be modified on the gold nanoparticles, promising a wide application of this copolymer-templated, gold-nanoparticles-modified, OFET-based sensor.

In addition to the aforementioned two cases where a current change was brought by the impact of binding events directly on the conducting channel, the gate voltage of an OFET device could also be affected by the host-guest binding of analytes, which indirectly resulted in an observation of current changes. Based on this strategy, in 1992, Reinhoudt *et al.* developed the ion-sensitive field effect transistor sensor based on calix[4]arene derivatives [57]. Recently, Palazzo and Torsi employed plasma enhanced vapor chemical deposition (PE-CVD) [58] to modify the poly(3-hexylthio-phene) (P3HT) semiconductor layer with carboxylic acids in a bottom-contact/ top-gate OFET [59]. Biotin was chosen as the binding site and was grafted on a phospholipid (PL) bilayers functionalized with amino groups. Thus, carboxylic acid groups can serve as the anchors to immobilize this biotinylated phospholipid bilayer at the interface between the gate and the P3HT active layer, leading to a sensing platform for streptavidin (Fig. **9a**). Because P3HT was a *p*-type semiconducting polymer, negative charges accumulated on the surface of the PL upon the induction of a negative gate bias. The binding of negatively charged streptavidin with biotins increased the negative charge density and strengthened the

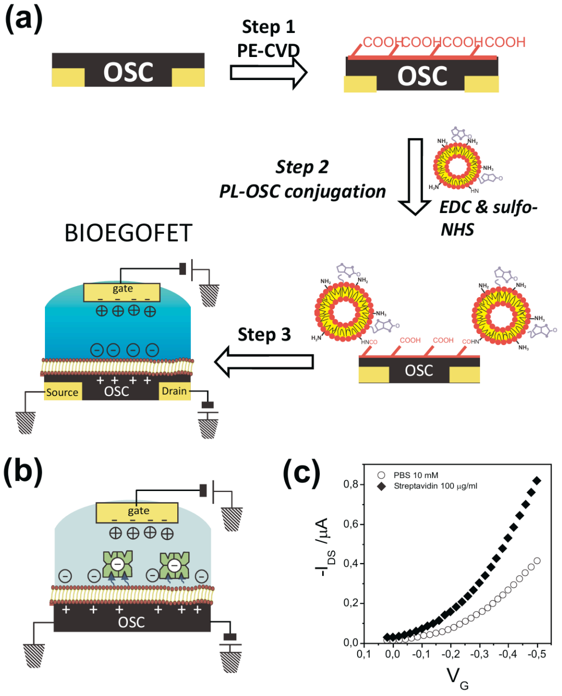

Fig. (9). a) Schematic view of the fabrication process of the top-gate OFET device. **b**) Graphical explanation of the formation of an extra electronic field. c) The current increase resulted from the binding event. [Adapted with permission from reference 59].

electric field. (Fig. **9b**) Consequently, an increased I_{DS} was measured as a signal readout. Such an increase of I_{DS} was absent when the device was exposed to other analytes or lacked the presence of biotins. (Fig. **9c**) Further investigation showed a logarithmic relationship between the fractional I_{DS} ($\Delta I/I_0$) and the concentration of streptavidin.

5. CONCLUSIONS AND PERSPECTIVE

The past decade has witnessed a significant advance in the field of supramolecular electronic sensors, exemplified by the highly selective and sensitive devices described above. The marriage between host-guest chemistry and electronic sensing technology rendered an excellent opportunity for the detection and analysis of chemical analytes in a highly efficient and feasible manner. In order to facilitate large-scale and real-life applications of these sensors, however, the scientists and engineers still need to address the issues related to device stability, reproducibility, reusability, reliability under extreme conditions, power consumption, and the cost of synthesis and fabrication. These challenges are interrelated with one another and require a combined effort associated with multiple research disciplines.

From a chemist's point of view, the construction of new active materials with tailored properties for electronic sensing is still of pivotal importance. A viable approach to more reliable and stable sensor materials, for example, could be the covalent attachment of supramolecular binding moieties onto conducting/semiconducting materials. Although it has been demonstrated that such covalent modification often damages the conductivity of the active materials [60], it is possible to balance the properties and functions through molecular engineering approaches such as copolymerization or side-chain modification [61]. Another interesting way to increase the sensitivity and throughput of the electronic sensors could be the employment of ordered yet conductive porous materials such as metal organic frameworks (MOFs) or covalent organic frameworks (COFs). The integration of conductivity and supramolecular entities with these materials are challenging but the future is bright. Recent groundbreaking developments of conductive COFs/MOFs [62, 63] supramolecular host-incorporated MOFs [64], and surface grown COFs [65] have paved the way to the next generation electronic sensing materials.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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