# Chemical and Engineering Approaches To Enable Organic Field-Effect Transistors for Electronic Skin Applications

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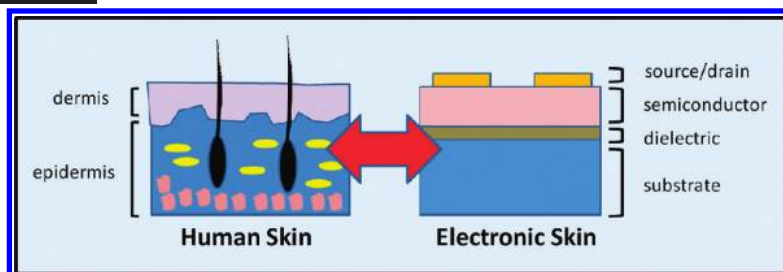
CONSPECTUS

Skin is the body's largest organ and is responsible for the transduction of a vast amount of information. This conformable material simultaneously collects signals from external stimuli that translate into information such as pressure, pain, and temperature. The development of an electronic material, inspired by the complexity of this organ is a tremendous, unrealized engineering challenge. However, the advent of carbon-based electronics may offer a potential solution to this long-standing problem.

In this Account, we describe the use of an organic field-effect transistor (OFET) architecture to transduce mechanical and chemical stimuli into electrical signals. In developing this mimic of human skin, we thought of the sensory elements of the OFET as analogous to the various layers and constituents of skin. In this fashion, each layer of the OFET can be optimized to carry out a specific recognition function. The separation of multimodal sensing among the components of the OFET may be considered a "divide and conquer" approach, where the electronic skin (e-skin) can take advantage of the optimized chemistry and materials properties of each layer.

This design of a novel microstructured gate dielectric has led to unprecedented sensitivity for tactile pressure events. Typically, pressure-sensitive components within electronic configurations have suffered from a lack of sensitivity or long mechanical relaxation times often associated with elastomeric materials. Within our method, these components are directly compatible with OFETs and have achieved the highest reported sensitivity to date. Moreover, the tactile sensors operate on a time scale comparable with human skin, making them ideal candidates for integration as synthetic skin devices. The methodology is compatible with large-scale fabrication and employs simple, commercially available elastomers.

The design of materials within the semiconductor layer has led to the incorporation of selectivity and sensitivity within gas-sensing devices and has enabled stable sensor operation within aqueous media. Furthermore, careful tuning of the chemical composition of the dielectric layer has provided a means to operate the sensor in real time within an aqueous environment and without the need for encapsulation layers.

The integration of such devices as electronic mimics of skin will require the incorporation of biocompatible or biodegradable components. Toward this goal, OFETs may be fabricated with >99% biodegradable components by weight, and the devices are robust and stable, even in aqueous environments. Collectively, progress to date suggests that OFETs may be integrated within a single substrate to function as an electronic mimic of human skin, which could enable a large range of sensing-related applications from novel prosthetics to robotic surgery.

Introduction

Skin is the body's largest organ and is responsible for the transduction of a vast amount of information. This conformable material simultaneously collects signals for pressure, pain, temperature and other information on the surrounding environment. The development of an electronic material inspired by the complexity of this organ is a tremendous engineering challenge. To date, soft and conformable materials capable of multimodal signal transduction with the precision of the natural organ have not been realized. To fulfill the roles carried out by human skin, novel approaches must be developed utilizing our understanding of chemistry and physics, coupled with innovative device integration strategies. However, the advent of carbon-based electronics has precipitated generally recognizable set of advantageous properties that may offer a potential solution to this long-standing problem. Carbon-based or organic electronic materials are not meant as a replacement for silicon-based devices but rather to fill complementary niches wherein versatile, low-cost, flexible materials compatible with large-area processing techniques are required.[1,2] Recent advances have positioned organic electronics to significantly impact light-emitting diodes (OLED),[3,4] sensors,[5,6] and photovoltaics.[7] This tremendous array of properties is accessed through the power of organic chemistry, because it provides a versatile approach to tune the materials toward a specific role.

It is with these concepts in mind that we outline, in this Account, the fundamental materials chemistry and device developments to enable materials capable of multimodal sensing. In particular, several multidisciplinary approaches to utilize an OFET as a basic building block to develop a material akin to electronic skin (e-skin) will be described. Nature's design of skin utilizes multiple components that operate in harmony within several layers and provide the tremendous range of functionality.[8,9] Herein, we demonstrate that each component of an OFET, namely, the semiconductor, dielectric, and substrate, may be individually "tuned" to achieve the necessary functionality to enable multimodal sensing. Finally, we discuss future strategies to integrate additional biocompatibility within the e-skin material.

A Concept of E-Skin

To approach the development of an electronic version of human skin, it is important to consider the fundamental chemistry and engineering requirements, as well as the applications envisioned. As the largest organ of the human body, skin is responsible for the transduction of physical

events occurring outside the body. These events can involve pressure, pain, and temperature recognition. A main driving area for these developments is robot/human interaction, replication of human tasks, minimally invasive surgery, and prosthetics.[10] Thus, initial development of applications will require that benchmarks in pressure sensing and in the use of biocompatible and biodegradable materials must be met. Additionally, skin functionality may be enhanced via incorporation of chemical or biological sensors for either gaseous or aqueous environments. This may be likened to the olfactory epithelium found in the nose or taste buds found on the tongue, which provide additional skin functionality. In all applications, the chosen material must be conformable and exhibit stability upon bending or potentially stretching events. Because skin is the largest organ, synthetic replication of human skin is well-suited for approaches that rely on functional, large area, flexible processing techniques and materials. For these reasons, there exists a great interest in the use of organic materials for developing e-skin.[11]

OFET as a Platform To Enable E-Skin

To address the individual modes of sensing exhibited by natural skin, we turn to the building block of organic electronics, namely, the OFET.[1] In this device, the flow of charges in the semiconductor layer between the source and drain terminals is regulated by the application of voltage on the third (gate) terminal. As mentioned, OFET devices comprised entirely of organic materials present tremendous advantages in cost, flexibility, chemical functionality, and compatibility with large area processing, demonstrating easily accessible device resolutions on the micrometer scale.[2,12] The typical pressure response resolution of natural skin is on the order of 40 μm,[10] a dimension accessible by a single OFET pixel. Currently, it is well-known that each OFET component plays a critical role in device performance.[13] These components involve active semiconductor materials, contacts, supporting substrates, dielectrics, and the interfaces between these materials. A great deal of progress has also been made in circuit, display, and sensor applications, among others.[11,14−21] There exists a tremendous amount of control over the properties of the OFET, accessed via chemical design and engineering of each component of the device. Therefore, the chemical and structural composition of each transistor constituent may be used to impart a separate sensing mode within the device. This vision is depicted in Figure 1, in which the dielectric layer is used as a pressure sensor and the active semiconductor layer as a chemical or biological species sensor, while
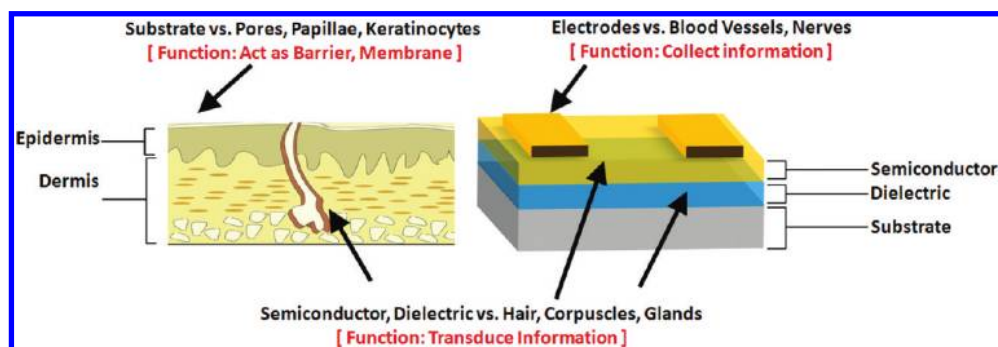
FIGURE 1. A schematic demonstrating multiple specifically "tuned" functional layers of human skin. Similarly, each layer of the OFET-based e-skin device is designed to carry out specific tasks akin to human skin.

incorporating biocompatible and biodegradable materials as device substrates.

Novel Materials Strategies To Enable Tactile Sensing for Organic Electronics

Arguably, one the most critical features of human skin is its ability to transduce tactile events. Pressure sensitivity is what allows humans to interact actively with the surrounding environment. On the surface of a human hand, >17 000 touch receptors must work in concert to transduce tactile information.[22] Natural pressure receptors are designed to provide varying amounts of sensitivity depending on location. Thus, the challenge in creating a pressure-sensitive e-skin is to provide a methodology toward pressure sensors with varying sensitivities over large areas. Pressure detection to rival human skin has been a subject of intense investigation in the past few years.[23−26] Recent materials chemistry and device requirements to achieve this goal have been reviewed.[10] However, we would like to highlight the first flexible and conformable pressure-sensitive material by Someya et al.[26] In this work, a pressure-sensitive elastomer was utilized as the sensor element to modulate the output current of an OFET. This allowed for a flexible and conformable material capable of uniform pressure recognition, even while bent to a radius of 2 mm. This work has motivated a string of subsequent investigations, with recent examples of macroscale, flexible materials operating at low voltages.[27]

We turned to exploiting the dielectric layer of the OFET to produce a pressure-sensitive response.[28] The primary consideration for tactile-sensitive element design was sensitivity toward low-pressure events. Because typical dielectric materials are incompressible oxides or polymers that do not significantly deform with pressure,[18,29] we chose to employ an elastomer (Figure 2a). An additional consideration for pressure sensors in e-skin applications is response time. The human physiological limit of sensation and thus the
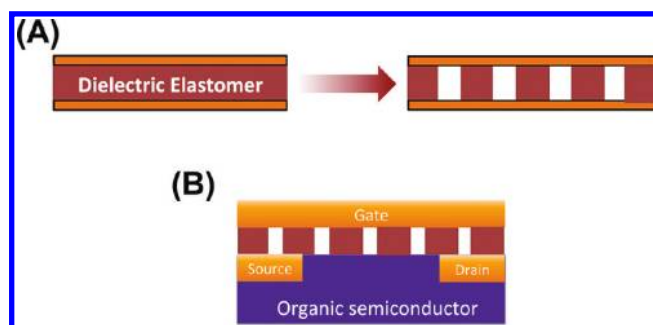

FIGURE 2. (A) A scheme of the microstructuring approach. (B) The microstructured material can then be applied as gate dielectric for an OFET structure.[28]

response time that must be achieved is ~100 ms.[30] An advantage to using a cross-linkable elastomer is the ability to tune the material properties. Thus, depending on the amount of cross-linker either a soft, easily deformable material with long relaxation times or a stiff material lacking sensitivity will be afforded.[31]

A novel approach in the form of microstructuring was used to take advantage of desirable elastomer properties.[28] This approach utilized soft lithography to create repeating features on the surface of a silicone elastomer, polydimethylsiloxane (PDMS), hence forming a highly ordered microstructured film. PDMS was chosen, because it is a well-understood, cross-linkable, nontoxic elastomer. The material may be cross-linked utilizing a platinum-catalyzed reaction between pendant vinyl and hydrogen-substituted siloxane groups distributed throughout the polymer chains.[32] An additional benefit is the reactivity of an oxidized PDMS surface (silanol groups) with trichlorosilanes, allowing for tunable surface chemistry. This approach may be likened to the introduction of highly ordered air gaps that lead to a foam-like material (Figure 2). During compression, the rubber fills the air pockets, leading to further increase in the overall dielectric permittivity of the film. By using the dielectric within a parallel plate structure, we are
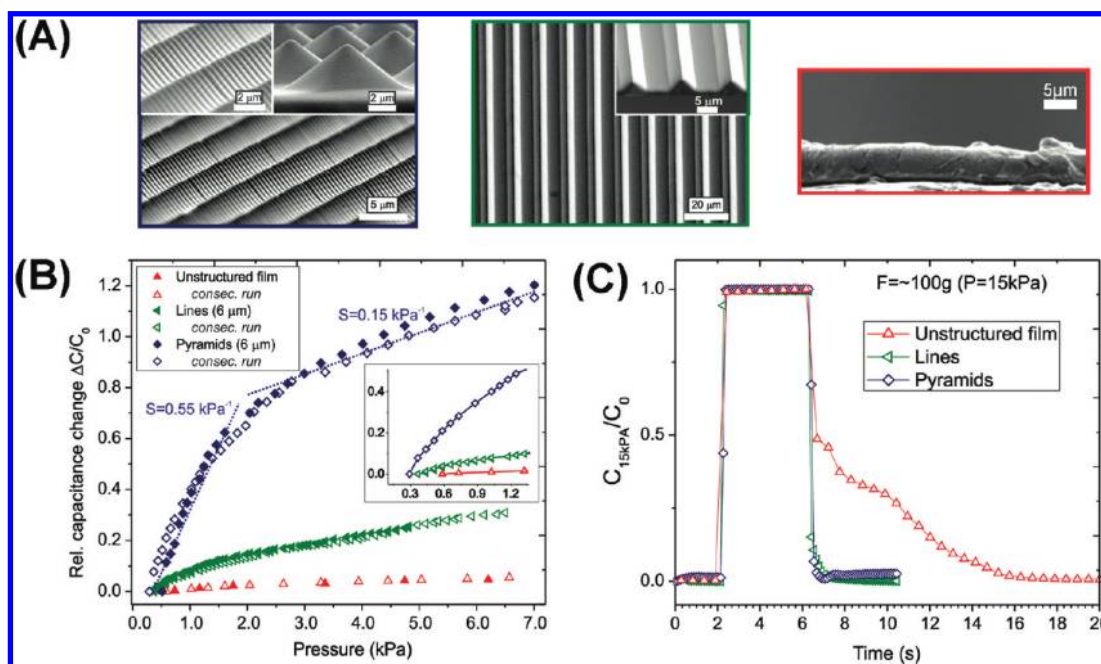
FIGURE 3. (A) Scanning electron microscopy images of structured pyramidal and line features and an unstructured cross-section of a PDMS film. (B) The static response of pyramidal (blue), line (green), and unstructured (red) PDMS films to static pressures. (C) Response vs time for applied dynamic pressure on pyramidal features (blue), line features (green), and unstructured (red) PDMS films.[28]

able to transduce pressure into an electronic (capacitance) signal.

When the relative capacitance change was compared for both the microstructured and unstructured thin films of the same thickness, the unstructured film exhibits little response even at higher pressure values of >5 kPa, while the microstructured films show a significant response at low pressure values of <2 kPa. Furthermore, the capacitance change also depends on the type of microstructures used (Figure 3A). When pyramidal structures were compressed, the initial capacitance change is as high as 55% kPa^{-1}, while a film with line patterns showed a smaller change. Nonetheless, the change is still ~5-fold larger than the comparable unstructured film. This observation indicates that using different types of microstructures can lead to varying pressure sensitivities, depending on the required application. This is comparable to human skin, wherein areas such as fingertips have higher sensitivities (a few kilopascals) than areas on a person's forearm. Application of dynamic pressure to the microstructured films demonstrates a tremendous increase in rate of response compared with unstructured films. In Figure 3B, the application of a pressure step function of 4 s is shown. While an unstructured film exhibits a significant delay time of ~5 s, both types of microstructured film exhibited rapid return of capacitance to the "off" state of ~100 ms. Thus, the lack of bulk film deformation

results in greatly improved response rate, while maintaining the elastomer properties (Figure 3C).

Flexibility and reliability are both important aspects of e-skins, especially for pressure sensors owing to constant mechanical contact with the environment. In Figure 4A, the flexibility of the microstructured film is demonstrated, showing reliable performance after >10 000 cycles of tensile and compressive strains. In addition, an *in situ* measurement of the capacitance during repeated flexing of the film to a 4-mm radius at 1 Hz did not show appreciable deterioration, demonstrating the robustness of the sensors. Temperature stability plays an important role in obtaining consistent information about the environment for both human and e-skin. When the temperature is increased, the microstructured dielectric is expected to undergo expansion, thus causing the capacitance to change. However, the change is reversible with temperature, as seen in Figure 4B. Furthermore, the change exhibits a linear relationship with different pressure values. This means that the sensor can be calibrated for quantitative/accurate determination of the applied pressure.

The use of a microstructuring approach endows the material with greatly enhanced tactile sensitivity when used in the parallel plate capacitor geometry. However, to utilize this material in e-skin, it is important to integrate the material within an OFET. To transform an OFET into a pressure sensor,
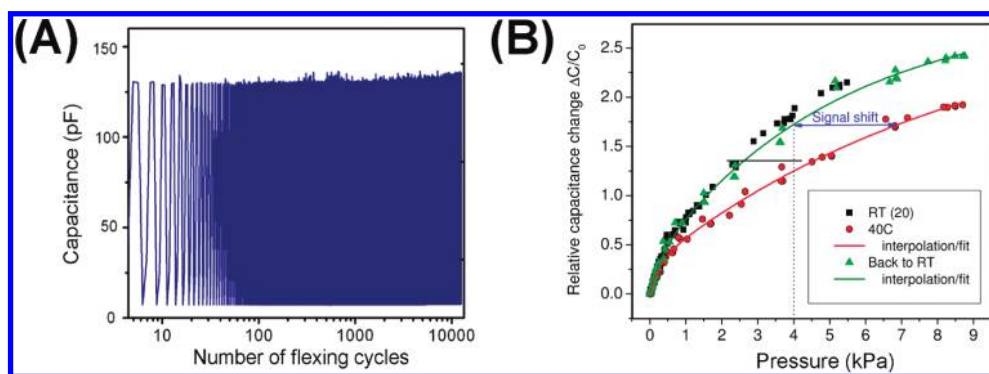
FIGURE 4. (A) Plot of the capacitance during the application of >10 000 flexing cycles showing sensor stability and (B) showing the signal shift in capacitance with temperature.[28]
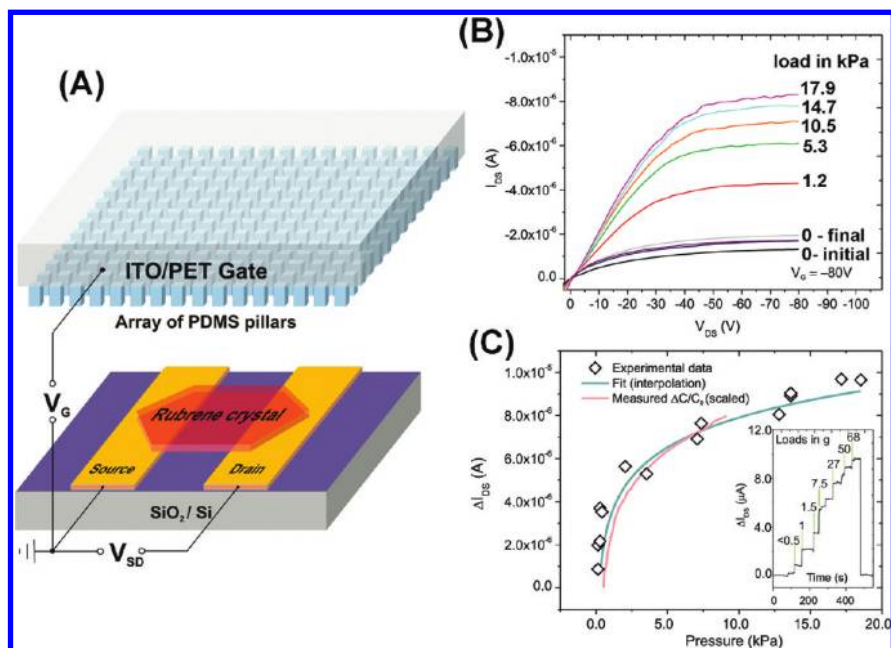

FIGURE 5. (A) A schematic showing the use of a single-crystal OFET for structured PDMS pressure sensors. (B) The electrical characteristics of the FET as a response to applied pressure. (C) A calibration plot showing the theoretical and experimental response of the FET to pressure, along with the capacitor response highlighting the fidelity of the electrical vs the capacitative signal.[28]

we applied the microstructured material as the gate dielectric laminated on top of a thin, flat rubrene crystal (Figure 5). At low pressure values (~1.2 kPa), the drain current is shown to have increased by >2-fold. At higher pressure values, the drain current increase per unit pressure decreases, in accordance with the capacitance. This plot is comparable to a typical OFET output plot; however, in this particular case, the increase in current is modulated by the applied pressure and not via applied gate voltage. The increase in current closely follows the increase in capacitance, indicating that the current is modulated by the capacitance changes of the dielectric material (Figure 5C). Even though this work demonstrated the feasibility of OFETs with elastomeric dielectrics for pressure sensing, further materials development

is still needed to replace the organic single crystal with organic semiconductor thin films or semiconducting carbon nanotubes.

In summary, by microstructuring elastomeric materials, we are able to retain the bulk elastic properties in PDMS films. In addition, varying pressure sensitivities can be obtained by using several types of microstructures. Thus, a method of making pressure sensors that mimic the broad range of tactile sensitivities found in human skin was provided. The thin, flexible microstructured material can subsequently be applied as the gate dielectric on organic semiconductors, imparting them with a "sense of touch". This initial integration demonstrates the possibilities of an OFET to drive the e-skin's components.
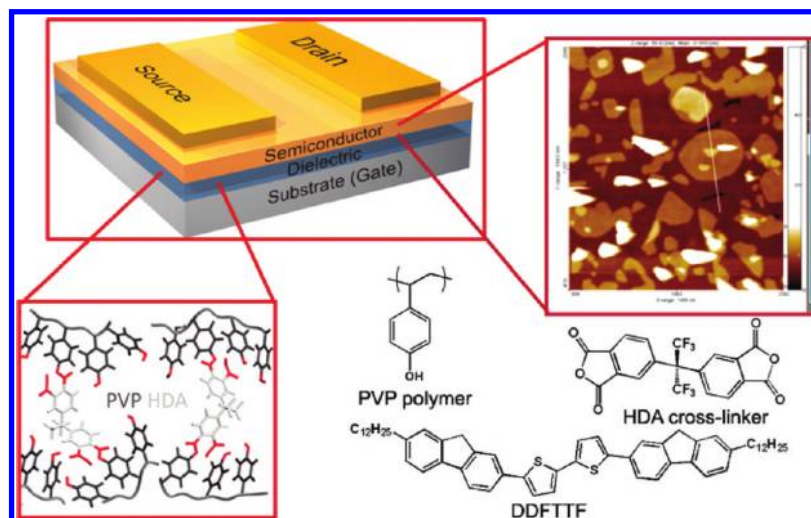
FIGURE 6. A schematic representation of the OFET highlighting the cross-linked poly(4-vinylphenol) (PVP) dielectric with the HDA (cross-linker) and the two-dimensional growth of the DDFTTF.[39]

Flexible OFET-Based Chemical and Biological Sensors for E-Skin

E-skin functionality will be enhanced by incorporation of chemical and biological sensors. We envisioned that the active layer of an OFET could be utilized to impart chemical sensitivity to the e-skin material. Chemical sensors based on OFETs have been shown to detect analytes in both gaseous and aqueous states.[6,11,17,33,34] Again, the semiconductor layer may be likened to the olfactory sensory neurons within the olfactory epithelium, with chemical functional groups acting as the "smell receptors" (gaseous sensing) or taste buds (aqueous sensing). These devices are particularly attractive owing to the use of the semiconductor as both the charge transport and the sensing layer. Additionally, sensors within transistor geometries present two specific advantages over comparable chemiresistors. First, the use of a gate electrode to modulate the current within the semiconductor has been shown to result in increased sensitivity to analytes.[35] Second, the transistors provide multiple parameters (e.g., mobility, threshold voltage) as read-out mechanisms of analyte detection.[36] Application of organic chemistry to provide chemically tailored receptor/sensing groups on the semiconductor can result in enhanced specificity and sensitivity.[15,37]

An initial goal for the development of OFETs, within the framework of e-skin, was operation and chemical detection within diverse media. To accomplish this goal, two requirements of OFET must be met. The first requirement to achieve stable operation within aqueous media, without special device encapsulation,[38,39] was low-voltage operation. The second requirement involved the design of a high-performance semiconductor material compatible with operation within the aqueous environment. We have recently reported on a system that has achieved both of these requirements (Figure 6).[39] The generation of a stable, cross-linked, ultrathin insulator allowed for transistor operation in the sub-1 V regime.[40] Operating below 1.23 V allows the transistor to avoid high ionic currents, while preventing the electrolysis of water during operation.[41] While other high capacitance, ultrathin dielectrics have been reported, these have not been used for aqueous sensors.[29,42] In our system, we utilized an air-stable, thermal cross-linking process between poly(4-vinylphenol) (PVP) and a dianhydride cross-linker (e.g., 4,4'-(hexafluoroisopropylidene)diphthalic anhydride, HDA).[39] This process maintained compatibility with flexible substrates (owing to the low thermal activation required to achieve cross-linking). The resultant films demonstrated low leakage currents and high capacitances that enabled transistor operation below the required 1.23 V.

For OFET operation under aqueous media (e.g., water, buffers, serums), we observed that the introduction of long alkyl chains (6−12 carbons) onto the periphery of organic semiconductors promoted stability.[39] This effect was attributed to hydrophobic side groups that effectively shield the organic semiconductor core from the water environment. The use of a dodecyl-substituted molecule, namely, 5,5'-bis-(7-dodecyl-9*H*-fluoren-2-yl)-2,2'-bithiophene (DDFTTF) has resulted in stable transistor operation in water for 12 h. The ability to operate an unencapsulated transistor within aqueous media opens up opportunities for *in situ* chemical detection.[39,43] Specifically, the OFET was utilized to detect part-per-million (ppm) to part-per-billion (ppb) concentrations
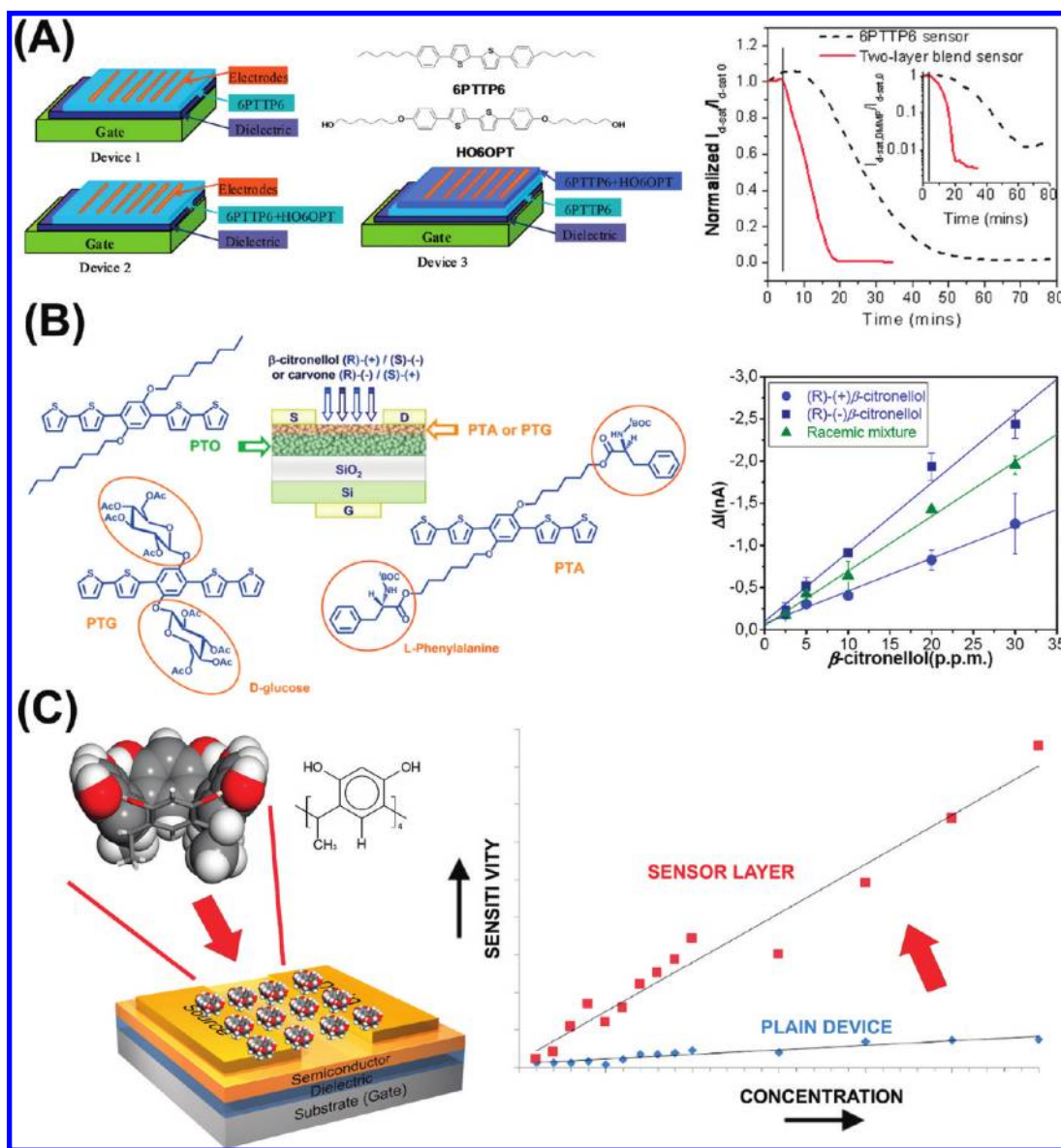
FIGURE 7. (A) Blend of functionalized semiconductor molecules by Katz et al. (Reprinted with permission from 46. Copyright 2011 American Chemical Society) (B) Chiral substituents for discrimination by Torsi et al.[15] (C) Our approach utilizing calix[n]arene sensing molecules and the response to a vapor.[37]

of small molecular analytes, ranging from explosive agents (trinitrotoluene (TNT)) to amino acids (cysteine), and changes in the pH of the local solution environment. The devices were also shown to function on flexible substrates with completely solution-processed components.[43] In addition to DDFTTF, a sorted network of carbon nanotubes was demonstrated to be another successful candidate for stable aqueous sensing.[40,44]

To address the selectivity requirement, it was shown that covalent attachment of receptor/sensing groups (e.g., hydroxyl or coordination groups) to organic semiconductors can lead to improved sensitivity and selectivity for certain analyte types (e.g., polar analytes, nitro groups, enantiomer

discrimination via chiral substituents on the sensor's semiconductor backbone) (Figure 7).[15,45,46] In the latter study, an impressive 3 ppm detection limit was observed with a 2-fold increase in response for the selected chiral component compared with the enantiomer at a concentration of 10 ppm. However, because introducing chemical substituents onto organic semiconductor structures can lead to a drastic change to its morphology, solubility, and ultimately, device performance, the use of this strategy would require an optimization of each device to achieve the required levels of sensor performance. Recently, we have developed an approach to circumvent the problem.[37] An additional sensory layer was deposited on the device surface by thermal

evaporation. We used "container-like" molecules based on calix[*n*]arenes, which are widely investigated as separation agents or building blocks in host−guest chemistry.[47] The cavity of the calix[*n*]arenes may be tuned via facile chemical synthesis. The introduction of an ultrathin layer of these molecules did not significantly impact the behavior of the OFET.

The devices were exposed to a series of volatile gaseous analytes at relatively high concentrations to establish the effects of the layers. The devices without calix[*n*]arene modification exhibited poor responses to the gaseous analyte, with no inherent selectivity or specificity for the solvent vapors. However, upon the introduction of a 2 nm layer of either calix[8]arene (C[8]A) or *c*-methylcalix[4]resorcinarene (CM[4]RA) molecules, a drastic increase in the response of the devices was observed (∼9-fold increase). The use of C[8]A as the sensory layer resulted in a specific selectivity for ethyl acetate, while CM[4]RA exhibited selectivity for isopropyl alcohol (Figure 7). In total, the use of the calix-[*n*]arenes improved both the device sensitivity and device selectivity over the nonfunctionalized device. Importantly, the increases were observed on the same semiconductor compound, demonstrating the capability to achieve multiplexed detection from a single OFET device architecture.

After selective detection of gaseous analytes, we turned to the detection of single-stranded (ss) DNA molecules[48] utilizing peptide nucleic acids (PNAs) as the receptor ligands.[49] ssPNA has previously been observed to form a tightly bound double helical structure with a complementary ssDNA strand and has been utilized in various DNA-sensing architectures.[50,51] We demonstrated for the first time that a ssPNA probe could detect complementary DNA (cDNA) sequences by an OFET *in situ* within buffer media. The use of this probe provided excellent chemical sensitivity (limit of detection ≈ 1 nM) and selectivity, because it is able to differentiate between strands comprised of merely a single base pair mismatch (Figure 8B). In this example, 2-fold and 4-fold increases in signal are observed for a single or a two base-pair mismatch, respectively. However, in contrast to optical detection techniques, this system can be fully integrated into increasingly complex electronic circuits to provide a rapid, large area, cheap screening platform for a variety of biological agents. Recently, a similar approach has been demonstrated for the detection of larger biological species (proteins, antibodies).[52]

These achievements demonstrate a highly important capability of the OFETs. The potential tunability of the materials to achieve improved performance should lead to increased sensor response sensitivities, as well as improved
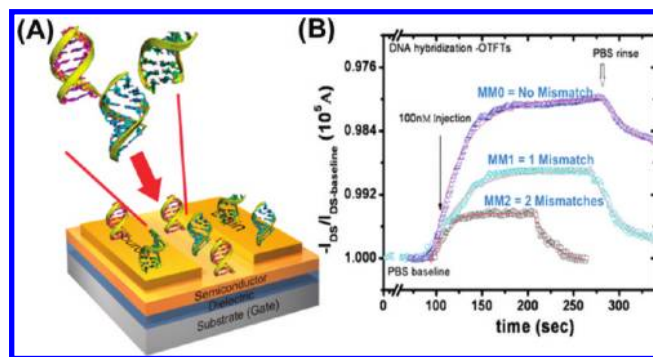

FIGURE 8. DNA sensing using OFET devices. (A) Schematic of PNA−DNA binding event on an OFET, and (B) plot demonstrating the response to a binding event of cDNA strands.[48]

compatibility with circuit integration. The integration of these individual sensory components as active pixels within a single material will be manifested as highly useful components of an e-skin. The ability to collect real time, *in situ* data for both gaseous and aqueous environments in contact with the e-skin will be a great asset for enhanced robotic surgery and military applications.

Biomaterial-Based Organic Electronics for Bridging the Biotic−Abiotic Gap

The sensitive tactile and thermal functions of human skin are a product of evolution that provide a basis for biomimicry in synthetic e-skin. Natural human skin exhibits a number of salient properties that serve as guidelines for the development of e-skin applications.[53] However, human skin is composed of an array of biomaterials-based structures that are engineered to transduce external stimuli into signals that can be interpreted by the nervous system. Synthetic e-skin that is intended to function as an orthotic device should ideally be synthesized using biocompatible, and even biodegradable, components.[54] This unmet need has driven the exploration of biomaterials as active and structural components in organic electronic devices.

Recent reports have focused on utilizing biodegradable or "naturally occurring" semiconducting molecules as active layers (Figure 9).[55] For example, cross-linked DNA has been utilized as a dielectric material[56] and β-carotene has been utilized as the active semiconducting layer.[57] Therefore, organic electronic systems that are fabricated on biocompatible elastomers may produce an improved tissue response and ultimately enhance integration of the device with the host.

Our initial efforts examined the use of biocompatible and biodegradable polymers, as substrates and insulators, while employing water-stable synthetic semiconductors as active
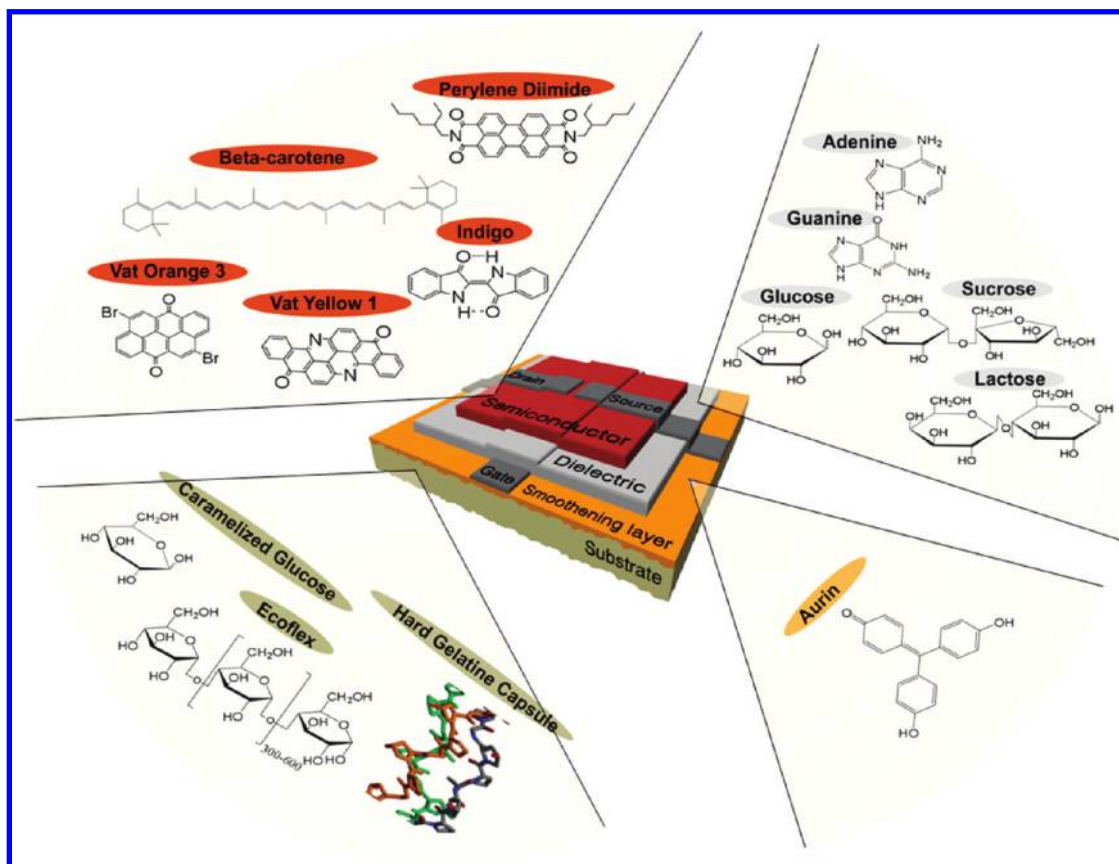
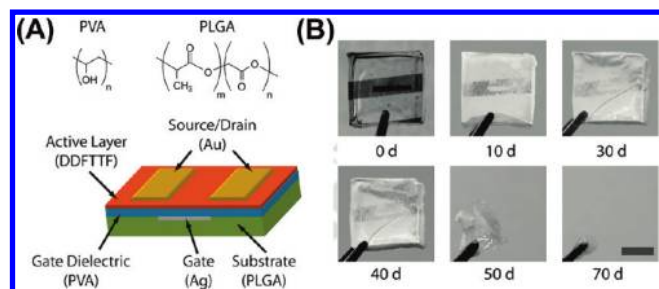**FIGURE 9.** Naturally occurring and bioinspired materials for use in OFETs.[55]

FIGURE 10. (A) Materials used in the fabrication of the biodegradable OFET. (B) Degradation of the OFET over a course of 70 days.[58]

layers (Figure 10).[58] Poly(vinyl alcohol) (PVA) and poly(L-lactide-*co*-glycolide) (PLGA) were utilized as the dielectric layer and substrate because of their biocompatibility and relevant biodegradation time scales.[56] These devices were fabricated into top-contact transistor structures, in which the substrate and dielectric make up >99% of the device mass. Thus, the use of other nontoxic metals or conductive polymer (<1%) should be compatible with these biodegradable devices. These devices functioned under water on the time scale of hours, and *in vitro* biodegradation studies revealed that the devices were significantly absorbed after 50 days.

The mass loss kinetics exhibited a traditional bulk degradation profile, which is attributed to the high content of PLGA in the device.

Generally, the interface between organic electronics and natural systems is an intriguing area of interest that could serve as key component in designing the "next generation" medical implants. For example, improved biocompatibility may be accomplished by incorporating biomolecules into the conducting polymer matrix to serve as adhesion ligands[59] or payload for controlled release.[60] These advances, in combination with the continual development of the OFET components, will ultimately lead to the realization of e-skin material.

Summary and Outlook

In this Account, we have outlined both the recent progress and general strategies to enable a synthetic material functioning akin to human skin. These developments will have broad significance in applications of e-skin prosthetics, in robotic-based minimally invasive surgeries, and in possible military applications. We focused on each layer of the OFET to demonstrate that proper performance levels for each

component can be achieved. In this fashion, each layer of the OFET functions akin to the varying layers of human skin. These components include both biocompatible and biodegradable transistors for eventual integration as a skin prosthetic. The advanced functionality, as imparted by chemical and biological sensing capabilities within the material, will enable novel e-skin applications. A novel microstructuring approach has allowed the OFET to behave as a pressure transducer with unprecedented sensitivity. Furthermore, the response time of these pressure-sensitive transistors is comparable with those of natural skin. The ability to optimize each material separately will make it easier to reach the final goal of single e-skin material integration. Continual development materials in the context of stretchable electronic devices will be the next critical step.[61] We also envision future e-skin may be powered with stretchable power sources, such as stretchable organic solar cells[62] and stretchable energy storage devices.[63,64] Additionally, each of these layers must eventually be manufactured via high-throughput techniques (e.g., printing). Thus, the challenge in the creation of the "next-generation" e-skin will be the continual optimization of the electronic device components within the scope of available materials chemistry and manufacturing processes.

BIOGRAPHICAL INFORMATION

Anatoliy N. Sokolov received both his B.S.E. in Electrical Engineering in 2003 and Ph.D. in Organic Chemistry in 2007 (with Leonard R. MacGillivray) from The University of Iowa, working on the design of supramolecular assemblies of organic semiconductors. He is currently a postdoctoral associate with Zhenan Bao at Stanford University, working on the development of sensors based on organic electronics.

Benjamin C-K. Tee received his B.S.E. in Electrical Engineering from The University of Michigan in 2006 and M.S. degree in Electrical Engineering from Stanford University in 2007. After a research stint in the Institute of Materials Research and Engineering (IMRE) in Singapore, he returned to Stanford University in 2008 to pursue his Ph.D. in Electrical Engineering with Zhenan Bao, under the National Science Scholarship (NSS) awarded by the Singapore Agency for Science Technology and Research (A*STAR). His main research interests are the fabrication, development, and application of sensors for flexible, stretchable e-skins.

Christopher Bettinger received his Ph.D. from MIT in 2008 as a Charles Stark Draper Fellow. After an NIH Ruth Kirschstein post-doctoral fellowship with Zhenan Bao (2008−2010), he is currently an Assistant Professor in both the Department of Materials Science and Engineering and the Department of Biomedical Engineering at Carnegie Mellon University. He has received many honors including the ACS AkzoNobel Award for Polymer Chemistry and the Tissue Engineering Society Young Investigator Award. He received a Ph.D. from MIT in 2008 as a Charles Stark Draper Fellow and a postdoctoral fellowship at Stanford University as an NIH Ruth Kirschstein Fellow in 2010.

Jeffrey Tok received his B.Sc. from The University of Washington at Seattle and Ph.D. from The University of Chicago. After a postdoctoral stay in Harvard, he has held positions as an Associate Professor of Chemistry in The City University of New York, York College and Graduate Center, as Principal Investigator in Lawrence Livermore National Laboratory, and as Chief Bioscientist in Micropoint Biosciences Inc. He is a Senior Research Scientist in Stanford since 2010. He has over 35 publications, received funding from NIH, ACS-PRF, etc., and was bestowed with several awards, including Nanotech Briefs 3rd Annual Nano-50 Technology Award (2007) and American Association for Cancer Research (AACR)-HBCU Faculty Scholar Award in Cancer Research (2002).

Zhenan Bao received her Ph.D. from University of Chicago. After spending 8 years in Bell Labs as a Distinguished Member of Technical Staff, she joined Stanford as an Associate Professor in 2004. She has over 200 refereed publications and 36 US patents. Selected recent awards include ACS Arthur Cope Scholar Award for 2011, ACS Fellow 2011, ACS PMSE Fellow in 2011, RSC Beilby Medal and Prize in 2009, SPIE Fellow in 2008, and IUPAC Creativity in Applied Polymer Science Prize in 2008.

REFERENCES

1 Bao, Z.; Locklin, J. *Organic Field-Effect Transistors*; Taylor & Francis Group: Boca Raton, FL, 2007.

2 Reese, C.; Roberts, M.; Ling, M.-M.; Bao, Z. Organic thin film transistors. *Mater. Today* **2004**, *7*, 20–27.

3 Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. G. Synthesis of light-emitting conjugated polymers for applications in electroluminescent devices. *Chem. Rev.* **2009**, *109*, 897–1091.

4 Walzer, K.; Maennig, B.; Pfeiffer, M.; Leo, K. Highly efficient organic devices based on electrically doped transport layers. *Chem. Rev.* **2007**, *107*, 1233–1271.

5 Torsi, L.; Dodabalapur, A. Organic thin-film transistors as plastic analytical sensors. *Anal. Chem.* **2005**, *77*, 381–387.

6 Roberts, M. E.; Sokolov, A. N.; Bao, Z. Material and device considerations for organic thin-film transistor sensors. *J. Mater. Chem.* **2009**, *19*, 3351–3363.

7 Thompson, B. C.; Fréchet, J. M. J. Polymer—fullerene composite solar cells. *Angew. Chem., Int. Ed.* **2008**, *47*, 58–77.

8 McKee, P. H. *Pathology of the Skin*; Lippincott: Philadelphia, 1989.

9 Goldsmith, L. A. *Biochemistry and Physiology of the Skin*; Oxford University Press: New York.

10 Maheshwari, V.; Saraf, R. Tactile devices to sense touch on a par with a human finger. *Angew. Chem., Int. Ed.* **2008**, *47*, 7808–7826.

11 Someya, T.; Dodabalapur, A.; Huang, J.; See, K. C.; Katz, H. E. Chemical and physical sensing by organic field-effect transistors and related devices. *Adv. Mater.* **2010**, *22*, 3799–3811.

12 Katz, H. E.; Huang, J. Thin-film organic electronic devices. *Annu. Rev. Mater. Res.* **2009**, *39*, 71–92.

13 Braga, D.; Horowitz, G. High-performance organic field-effect transistors. *Adv. Mater.* **2009**, *21*, 1473–1486.

14 Wu, Y. L.; Li, Y. N.; Ong, B. S. Printed silver ohmic contacts for high-mobility organic thin-film transistors. *J. Am. Chem. Soc.* **2006**, *128*, 4202–4203.

15 Torsi, L.; Farinola, G. M.; Marinelli, F.; Tanese, M. C.; Omar, O. H.; Valli, L.; Babudri, F.; Palmisano, F.; Zambonin, P. G.; Naso, F. A sensitivity-enhanced field-effect chiral sensor. *Nat. Mater.* **2008**, *7*, 412–417.

16 Wang, J. Z.; Gu, J.; Zenhausem, F.; Sirringhaus, H. Low-cost fabrication of submicron all polymer field effect transistors. *Appl. Phys. Lett.* **2006**, *88*, No. 133502.

17 Mabeck, J. T.; Malliaras, G. G. Chemical and biological sensors based on organic thin-film transistors. *Anal. Bioanal. Chem.* **2006**, *384*, 343–353.

18 Veres, J.; Ogier, S.; Lloyd, G.; de Leeuw, D. Gate insulators in organic field-effect transistors. *Chem. Mater.* **2004**, *16*, 4543–4555.

19 Lee, J.; Panzer, M. J.; He, Y.; Lodge, T. P.; Frisbie, C. D. Ion gel gated polymer thin-film transistors. *J. Am. Chem. Soc.* **2007**, *129*, 4532–4533.

20 Gelinck, G. H.; Huitema, H. E. A.; van Veenendaal, E.; Cantatore, E.; Schrijnemakers, L.; van der Putten, J. B. P. H.; Geuns, T. C. T.; Beenhakkers, M.; Giebers, J. B.; Huisman, B.-H.; Meijer, E. J.; Benito, E. M.; Touwslager, F. J.; Marsman, A. W.; van Rens, B. J. E.; de Leeuw, D. M. Flexible active-matrix displays and shift registers based on solution-processed organic transistors. *Nat. Mater.* **2004**, *3*, 106–110.

21 Rogers, J. A.; Bao, Z.; Baldwin, K.; Dodabalapur, A.; Crone, B.; Raju, V. R.; Kuck, V.; Katz, H.; Amundson, K.; Ewing, J.; Drzaic, P. Paper-like electronic displays: Large-area rubber-stamped plastic sheets of electronics and microencapsulated electrophoretic inks. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 4835–4840.

22 Vallbo, A. B.; Johansson, R. S. Properties of cutaneous mechanoreceptors in the human hand related to touch sensation. *Hum. Neurobiol.* **1984**, *3*, 3–14.

23 Manunza, I.; Bonfiglio, A. Pressure sensing using a completely flexible organic transistor. *Biosens. Bioelectron.* **2007**, *22*, 2775–2779.

24 Lee, H.-K.; Chang, S.-I.; Yoon, E. A flexible polymer tactile sensor: Fabrication and modular expandability for large area deployment. *J. Microelectromech. Syst.* **2006**, *15*, 1681–1686.

25 Darlinski, G.; Böttger, U.; Waser, R.; Klauk, H.; Halik, M.; Zschieschang, U.; Schmid, G.; Dehm, C. Mechanical force sensors using organic thin-film transistors. *J. Appl. Phys.* **2005**, *97*, No. 093708.

26 Someya, T.; Sekitani, T.; Iba, S.; Kato, Y.; Kawaguchi, H.; Sakurai, T. A large-area, flexible pressure sensor matrix with organic field-effect transistors for artificial skin applications. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 9966–9970.

27 Takei, K.; Takahashi, T.; Ho, J. C.; Ko, H.; Gillies, A. G.; Leu, P. W.; Fearing, R. S.; Javey, A. Nanowire active-matrix circuitry for low-voltage macroscale artificial skin. *Nat. Mater.* **2010**, *9*, 821–826.

28 Mannsfeld, S. C. B.; Tee, B. C. K.; Stoltenberg, R. M.; Chen, C.; Barman, S.; Muir, B. V. O.; Sokolov, A. N.; Reese, C.; Bao, Z. Highly sensitive flexible pressure sensors with microstructured rubber dielectric layers. *Nat. Mater.* **2010**, *9*, 859–864.

29 Facchetti, A.; Yoon, M.-H.; Marks, T. J. Gate dielectrics for field-effect transistors: new opportunities for organic electronics. *Adv. Mater.* **2005**, *17*, 1705–1725.

30 Johansson, R. S.; Flanagan, J. R. Coding and use of tactile signals from the fingertips in object manipulation tasks. *Nat. Rev. Neurosci.* **2009**, *10*, 345–359.

31 Schneider, F.; Fellner, T.; Wilde, J.; Wallrabe, U. Mechanical properties of silicones for MEMS. *J. Micromech. Microeng.* **2008**, *18*, No. 065008.

32 James, P. M.; Barrall, E. M.; Dawson, B.; Logan, J. A. Cross-linking of methyl silicone rubbers. Part 11. Analysis of extractables from samples cross-linked under various conditions. *J. Macromol. Sci., Chem.* **1974**, *A8*, 135–155.

33 Torsi, L.; Dodabalapur, A.; Sabbatini, L.; Zambonin, P. G. Multi-parameter gas sensors based on organic thin-film-transistors. *Sens. Actuators, B* **2000**, *67*, 312–316.

34 Sokolov, A. N.; Roberts, M. E.; Bao, Z. Fabrication of low-cost electronic biosensors. *Mater. Today* **2009**, *12*, 12–20.

35 Tanese, M. C.; Fine, D.; Dodabalapur, A.; Torsi, L. Interface and gate bias dependence responses of sensing organic thin-film transistors. *Biosens. Bioelectron.* **2005**, *21*, 782–788.

36 Liao, F.; Chen, C.; Subramanian, V. Organic TFTs as gas sensors for electronic nose applications. *Sens. Actuators, B* **2005**, *107*, 849–855.

37 Sokolov, A. N.; Roberts, M. E.; Johnson, O. B.; Cao, Y.; Bao, Z. Induced sensitivity and selectivity in thin film transistor sensors via calixarene layers. *Adv. Mater.* **2010**, *22*, 2349–2353.

38 Someya, T.; Dodabalapur, A.; Gelperin, A.; Katz, H. E.; Bao, Z. Integration and response of organic electronics with aqueous microfluidics. *Langmuir* **2002**, *18*, 5299–5302.

39 Roberts, M. E.; Mannsfeld, S. C. B.; Queralto, N.; Reese, C.; Locklin, J.; Knoll, W.; Bao, Z. Water-stable organic transistors and their application in chemical and biological sensors. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 12134–12139.

40 Roberts, M. E.; LeMieux, M. C.; Bao, Z. Sorted and aligned single-walled carbon nanotube networks for transistor-based aqueous chemical sensors. *ACS Nano* **2009**, *10*, 3287–3293.

41 Harris, D. C. *Quantitative Chemical Analysis*, 6th ed.; W. H. Freeman and Company: New York, 2003.

42 Halik, M.; Klauk, H.; Zschieschang, U.; Schmid, G.; Dehm, C.; Schutz, M.; Maisch, S.; Effenberger, F.; Brunnbauer, M.; Stellacci, F. Low-voltage organic transistors with an amorphous molecular gate dielectric. *Nature* **2004**, *431*, 963–966.

43 Roberts, M. E.; Mannsfeld, S. C. B.; Stoltenberg, R. M.; Bao, Z. Flexible, plastic transistor-based chemical sensors. *Org. Electron* **2008**, *10*, 377–383.

44 Roberts, M. E.; LeMieux, M. C.; Sokolov, A. N.; Bao, Z. Self-sorted nanotube networks on polymer dielectrics for low-voltage thin-film transistors. *Nano Lett.* **2009**, *9*, 2526–2531.

45 Dudhe, R. S.; Tiwari, S. P.; Raval, H. N.; Khaderbad, M. A.; Singh, R.; Sinha, J.; Yedukondalu, M.; Ravikanth, M.; Kumar, A.; Rao, V. R. *Appl. Phys. Lett.* **2008**, *93*, No. 263306.

46 Huang, J.; Miragliotta, J.; Becknell, A.; Katz, H. E. Hydroxy-terminated organic semi-conductor-based field-effect transistors for phosphonate vapor detection. *J. Am. Chem. Soc.* **2007**, *129*, 9366–9376.

47 Atwood, J. L.; Steed, J. W. *Encyclopedia of Supramolecular Chemistry*; CRC Press: Boca Raton, FL, 2004; Vol. 2.

48 Khan, H. U.; Roberts, M. E.; Johnson, O. B.; Förch, R.; Knoll, W.; Bao, Z. In-Situ, label-free DNA detection using organic transistor sensors. *Adv. Mater.* **2010**, *22*, 4452–4456.

49 Nielsen, P. E. PNA technology. *Mol. Biotechnol.* **2004**, *26*, 233–248.

50 Patolsky, F.; Lieber, C. M. Nanowire nanosensors. *Mater. Today* **2005**, *8*, 20–28.

51 Mirkin, C. A.; Letsinger, R. L.; Mucic, R. C.; Storhoff, J.J. A DNA-based method for rationally assembling nanoparticles into macroscopic materials. *Nature* **1996**, *383*, 607–609.

52 Khan, H. U.; Jang, J.; Kim, J.-J.; Knoll, W. In-situ antibody detection and charge discrimination using aqueous stable pentacene transistor biosensors. *J. Am. Chem. Soc.* **2011**, *133*, 2170–2176.

53 Yannas, I. V.; Burke, J. F.; Orgill, D. P.; Skrabut, E. M. Wound tissue can utilize a polymeric template to synthesize a functional extension of the skin. *Science* **1982**, *215*, 174–176.

54 Kim, D.-H.; et al. Dissolvable films of silk fibroin for ultrathin conformal bio-integrated electronics. *Nat. Mater.* **2010**, *9*, 511–517.

55 Irimia-Vladu, M.; et al. Biocompatible and biodegradable materials for organic field-effect transistors. *Adv. Funct. Mater.* **2010**, *20*, 4069–4076.

56 Yumusak, C.; Singh, T. B.; Sariciftci, N. S.; Grote, J. G. Bio-organic field effect transistors based on crosslinked deoxyribonucleic acid (DNA) gate dielectric. *App. Phys. Lett.* **2009**, *95*, No. 263304.

57 Burch, R. R.; Dong, Y.-H.; Fincher, C.; Goldfinger, M.; Rouviere, P. E. Electrical properties of polyunsaturated natural products: field effect mobility of carotenoid polyenes. *Synth. Met.* **2004**, *146*, 43–46.

58 Bettinger, C. J.; Bao, Z. Organic Thin-Film Transistors Fabricated on Resorbable Biomaterial Substrates. *Adv. Mater.* **2010**, *22*, 651–655.

59 Gomez, N.; Schmidt, C. E. Nerve growth factor-immobilized polypyrrole: Bioactive electrically conducting polymer for enhanced neurite extension. *J. Biomed. Mater. Res.* **2007**, *81A*, 135–149.

60 George, P. M.; LaVan, D. A.; Burdick, J. A.; Chen, C. Y.; Liang, E.; Langer, R. Electrically controlled drug delivery from biotin-doped conductive polypyrrole. *Adv. Mater.* **2006**, *18*, 577–581.

61 Wagner, S.; Lacour, S. P.; Jones, J.; Hsu, P.-h. I.; Sturm, J. C.; Li, T.; Suo, Z. Electronic skin: Architecture and components. *Phys. E* **2004**, *25*, 326–334.

62 Lipomi, D. J.; Tee, B.C.-K.; Vosgueritchian, M.; Bao, Z. Stretchable organic solar cells. *Adv. Mater.* **2011**, *23*, 1771–1775.

63 Kaltenbrunner, M.; Kettlgruber, G.; Siket, C.; Schwödiauer, R.; Bauer, S. Arrays of ultracompliant electrochemical dry gel cells for stretchable electronics. *Adv. Mater.* **2010**, *22*, 2065–2067.

64 Yu, C. J.; Masarapu, C.; Rong, J. P.; Wei, B. Q.; Jiang, H. Q. Stretchable supercapacitors based on buckled single-walled carbon nanotube macrofilms. *Adv. Mater.* **2009**, *21*, 4793–4797.