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The Potential of Molecular Self-Assembled Monolayers in Organic Electronic Devices

Marcus Halik* and Andreas Hirsch

Functionalized molecules that organize to self-assembled monolayers (SAMs) are gaining importance in organic electronic devices. They are fully compatible with flexible substrates, are amenable to low-cost processing, and show reliable film-forming behavior. Highly integrated devices, such as sensor arrays or memories, have also been demonstrated. Starting from auxiliary layers, which improve and modify surfaces and interfaces in traditional thin-film devices, the applications of SAMs develop towards molecular scale electronics, including active molecular device layers and multifunctional SAMs, which fulfill several layer functions of a device within one monolayer. Mixed SAMs make new and tunable device features possible, by stoichiometric control of the composition of different SAM-forming molecules.

1. Introduction

A closer look at the most successful engineering approach in nature's manufacturing shows that the construction of complex living architectures takes place simply by hierarchical self-organization. This self-assembly occurs virtually unaffected by gravity, temperature gradients, magnetic fields, or other external stimuli in three dimensions in an extraordinarily reliable way. A molecular building block seems to know "when", "where", and "how" to assemble in the right order and the right time to create highly specific and diverse functional structures with a three-dimensional (3D) spatial resolution on the nanometer scale. Engineers and material scientists are very eager to simply copy these approaches to realize functional structures by means of these construction methods.

Since the discovery of organic electronic devices in the late 1980s and the successful introduction of their typical electronic key elements – organic thin-film transistors (OTFTs), organic light-emitting diodes (OLEDs), organic photovoltaic (OPV) cells, or organic memory (OMEM) cells – many of them have already reached or are close to first market applications in displays,

flexible solar panels, or integrated circuits. The most propagated "advantages" of organic electronics compared to their inorganic counterparts are related to potential low-cost and low-temperature processing by printing or other solution-based processes, or to large-area applications on flexible substrates. However, all organic electronic devices depend in at least one dimension on a high accuracy of molecular arrangement down to the nanometer or molecular scale, which is not automatically a feature of low-cost and large-area production processes. Molecular self-assembly could be a key enabler for organic electronics, because it combines the advantages of low-

temperature solution deposition methods, regio-selective monolayer adsorption and angstrom-scale control of the film thickness. Tremendous progress has been achieved in device performance and smart processing techniques with self-assembled monolayers (SAMs), which act as auxiliary layers in classical thin-film devices.^[1] During recent years, the use of SAMs that serve as or are part of an active device layer was established, providing functional mono- or multilayers on the molecular scale.^[1b,2] First attempts were made with multifunctional molecular SAMs, in which several device functionalities (layers) are incorporated into the molecular structure of a SAM or a SAM is the key active layer in the devices.^[3] A new research trend targets mixed monolayers and makes extended and tunable device characteristics possible.^[4] Additionally, more highly integrated systems of increased complexity or systems with increased mechanical stability were demonstrated^[2c,3b,5] and refute one of the major concerns regarding SAMs as active layers in devices: The question of reliability and robustness! In **Figure 1**, the general structures for functional SAMs, functional multilayers, multifunctional SAMs, and mixed SAMs are illustrated.

2. The Self-Assembly of Monolayers

The structure of molecules that tend to self-assemble on surfaces can be described as asymmetrical molecules with a surface reactive functional group (anchor group) **A** connected to a chained tail **T** and end capped with a head group **H** (see Figure 1). For all three subunits a wide variety of chemical structures have been demonstrated.^[1] Symmetric molecules (**A** = **H**) can also be used for self-assembly on surfaces and allow a controlled layer-by-layer growth, but they show a tendency to double-bond with the surface and thus have less-controlled layer properties.^[6]

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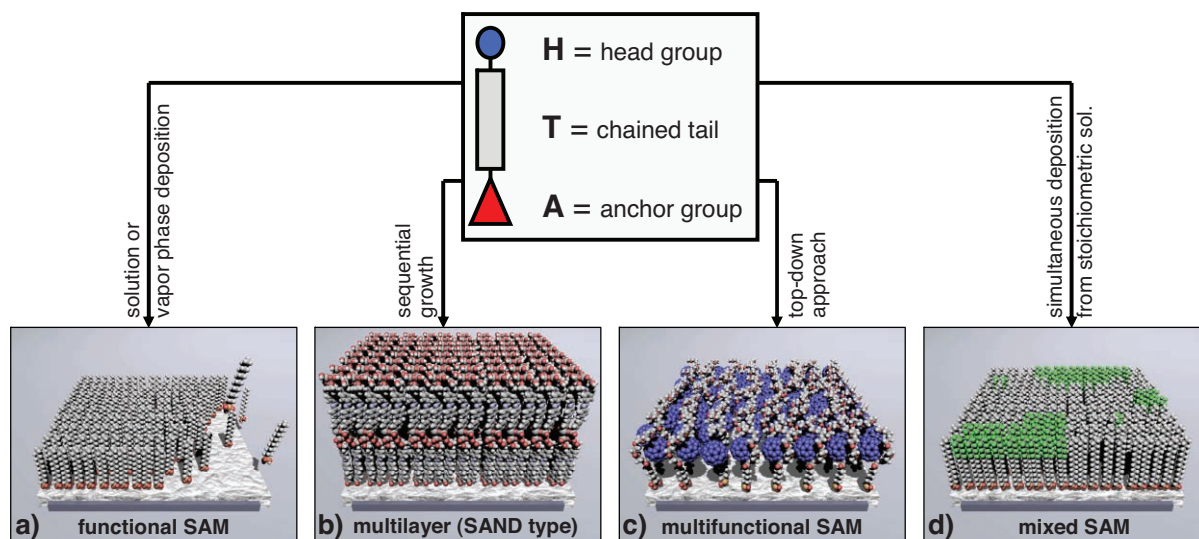


Figure 1. Schematic sketch of self-assembling molecules consisting of anchor, tail, and head. Schematic structure of a) the self-assembly of an *n*-alkylphosphonic acid as a functional SAM;^[2c] b) a functional multilayer of self-assembled nanodielectric (SAND) type;^[2d] c) a multifunctional SAM (glycol- C_{60} - C_6 -PA), where PA is phosphonic acid;^[3d] and d) a mixed SAM (HC_{18} -PA and FC_7 - HC_{11} -PA).^[4a]

Typical chain lengths of these molecular structures vary in the range of 0.5–5 nm, thereby indicating that a certain aspect ratio is favorable for self-assembly.

Dedicated reactive anchor groups, which selectively interact with corresponding surfaces, lead to a full coverage of those surfaces. Molecules with only one binding site ($A \neq H$) form a self-terminating arrangement to exactly one monolayer, which provides a precise layer thickness control of the resulting SAM arising from the length of the molecules and the tilt angle to the surface.^[7] In organic electronics, the choice of surfaces that can be treated with SAMs is rather limited to electrodes, dielectrics, and organic semiconductors. Additionally, SAMs can be used in advanced fabrication methods to create structural features on device substrates. Electrical contacts are mostly created from noble metals (e.g., Au, Ag, Pt, Pd), base metals, which typically tend to create native oxide layers (e.g., Al, Ti), transparent conductive oxides (e.g., indium tin oxide (ITO), doped ZnO), or conductive polymers (e.g., poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)).^[1a–f] In OTFTs the dielectric layer plays an important role in SAM applications. The most frequently investigated surface is silicon dioxide (SiO_2) treated with reactive silanes ($-SiCl_3$, $-Si(OR)_3$ or $-SiCl(OR)_2$), but also inorganic dielectrics with larger permittivity (e.g., AlO_x , HfO_x) and, of course, polymer dielectrics (e.g., poly(methylmethacrylate) (PMMA), poly(4-vinylphenol) (PVP)) are of importance, as well.^[1b] Some results have been published in which organic SAMs are coupled directly to the organic semiconductor and introduce sensor functionality of the devices.^[1g] It is notable that several materials need to be activated in order to provide a suitable density of reactive groups on their surface. Most prominent is the treatment with oxygen plasma or UV/ozone to create hydroxyl groups.

The relatively long molecular tail **T** typically dominates the electrical properties of the SAMs. The simplest and most investigated examples are functionalized *n*-alkanes of different chain lengths with insulating behavior. Also, fully conjugated systems consisting of various chain structures have been described (e.g., *p*-phenylene, phenylene-vinylene, phenylene-acetylene, oligo-thiophenes, or

acenes) as well as mixed approaches, combining conjugated and non-conjugated patterns.^[1,2] Several methods have been developed to investigate the properties of the SAM-forming molecules (e.g., molecular break junctions, scanning tunneling microscopy), small molecular assemblies of several molecules (e.g., nanopores, SAM-coated crossed wires), and larger SAM areas (e.g., metal–insulator–metal (MIM), metal–insulator–semiconductor (MIS)).^[2a] The capacitor approaches provide the most useful insight into SAM properties for organic electronic applications, because they cover the large scale (e.g., channel area) and they include the impact of potential defects on the SAM.^[2b–e,4,6]

The molecular head groups **H** determine the physical and chemical interaction of the SAM with the subsequently deposited layer or can directly act as active device layer. Groups that have been introduced into self-assembling molecules vary from simple methyl groups, fluoro-alkyl groups, and functional groups (e.g., $-NR_2$, $-OH$, $-SH$, $-COOH$) to aromatic and heteroaromatic groups.^[1,2] Newer research focuses on complex head groups, such as conjugated oligomers, or bulky groups, for instance C_{60} moieties.^[3a–d] Two general procedures have been described to introduce these head groups. Most commonly, the SAM-forming molecule is synthesized by a chemical routine in the lab and then deposited on the surface (top-down), or a reactive precursor is deposited on the surface and then sequentially converted to the final SAM structure (bottom-up). Solution-based deposition methods (e.g., rinsing, dip-coating, or printing) and vapor-phase processes have been described for both approaches and facilitate a large variability in the manufacture of functional SAMs.^[1]

3. SAMs as Auxiliary Layers in Organic Electronic Devices

SAMs on various materials enable full control and possible tuning of the materials' surface energy and they impact on the

morphology of the next sequentially deposited device layer and also on the device characteristics. Most prominent is the surface treatment of SiO₂ with *n*-octadecyltrichlorosilane (OTS) or hexamethyldisilazane (HMDS), which results in covalently bonded layers with low surface energy and tends to improve the crystallinity of various organic semiconductors (e.g., pentacene, C₆₀, oligothiophenes). An impressive example is the regioselective growth of organic single crystals on an OTS pattern on SiO₂, which is created by micro contact printing (μ -CP).^[1k] Several other silane-based molecules have been tested, and the concept has been extended to other anchor groups (e.g., phosphonic acid (–PO(OH)₂), carboxylic acid (–COOH)), which tend to self-assemble on other oxide surfaces (e.g., AlO_x, ITO, TiO₂).^[2c,d,3d,e,4] DiBenedetto et al. from Northwestern University and Virkar et al. from Stanford University have published excellent reviews in which the most common approaches and molecular structures are summarized.^[1b,f] Recent literature indicates that one major trend in SAM surface treatment targets a controlled growth or orientation of semiconductors not only by tuning the surface energy but also by using functionalized molecules. For example, Liao et al. have demonstrated improved mobility (up to 4.7 cm² V^{–1} s^{–1}) in pentacene TFTs, which is due to the larger crystalline domains of thermally evaporated pentacene films induced by π -interactions of different substituted anthracene phosphonates acting as SAMs on SiO₂.^[8a] Opatkiewicz et al. have used the approach of functional SAM surface treatment (amine surface at different pH values) to align single-walled carbon nanotubes (SWCNTs).^[1i] However, for polycrystalline organic semiconductors several issues are of further interest: the achievement of stronger orientation of crystalline domains, preferably along the TFT channel, and the identification of suitable head groups for the controlled nucleation of high-performance materials such as rubrene. Induced crystallinity of polycrystalline or semicrystalline polymer semiconductors was also achieved by treating source and drain (S/D) contacts with different thiols.^[1j] The concept is not limited to TFTs, but was also adapted for OPV and LED devices, in which the focus is on tuning of the injection barriers.^[1a,h]

4. SAMs as Device Layers

In 2000, Vuillaume's group in Lille, France, demonstrated that a single layer of carboxyl-terminated *n*-alkylsilanes on natively oxidized silicon can serve as a molecular dielectric layer in TFTs with a thickness of a few nanometers and with relatively low leakage current.^[2f] During the following years, the concept was extended to other molecules and high-mobility devices.^[2b–e] The most beneficial feature of this concept is the resulting low-voltage operation owing to the large capacitance $C \approx 0.9 \mu\text{F cm}^{-2}$ ($V_{\text{GS}} = Q/C = Qd/\epsilon\epsilon_0$, where V_{GS} is the gate–source voltage, Q is the charge density, and d and ϵ are the thickness and permittivity of the dielectric, respectively).^[2b] SAM dielectrics have been formed on ITO or Al (on Al the SAM creates a hybrid dielectric layer consisting of an AlO_x layer a few nanometers thick and the SAM, Figure 1a), thereby allowing fully integrated devices and circuits of p- and n-type semiconductors on rigid and flexible substrates.^[2c] A second concept that is based on controlled step-by-step assembly of molecules to self-assembled

nanodielectrics (SANDs), as shown in Figure 1b, results also in low-voltage operation with very low leakage current and a large capacity ($C \approx 0.4\text{--}0.7 \mu\text{F cm}^{-2}$, depending on the composition).^[1b,2d] For SAMs and SANDs, vapor-phase and solution-based processes have been developed,^[2d,e] and in general SAMs can be selectively deposited by μ -CP. Recent work focuses on a deeper understanding of the relationship between SAM structure and device performance and on discussing the impact of chain lengths, intermolecular organization, thermal stability, and chemical composition.^[8b–d] Since the observations by Kobayashi et al., which show that the dipole of a SAM (on SiO₂) shifts the threshold voltage in TFTs, SAM treatment has become an interesting tool for tuning V_{TH} , favorably close to 0 V, which is essential for effective circuitry.^[9a,b] Fluorinated and hydrocarbon dodecylphosphonic acids (FC₁₂-PA and HC₁₂-PA) in AlO_x/SAM hybrid dielectrics shift V_{TH} in pentacene or F₁₆CuPc TFTs by 1.0–1.2 V, which is almost half of the supply voltage that is necessary for the operation of the TFTs.^[9c]

In addition to SAM-based dielectrics for TFT applications, first examples of self-assembled monolayer field effect transistors (SAMFETs) have been demonstrated, in which the TFT semiconductor layer is created from a SAM that is directly attached to the dielectric interface (AlO_x of 100 ± 25 nm or thermally grown SiO₂ of 200 nm thickness).^[3a–c] Since the charge transport is limited to a monolayer, a dense packaging, namely an effective π -interaction of the semiconductor, is required. These early examples, made of silane-bonded oligothiophenes (4T and 5T), rely on short-channel devices ($L < 1 \mu\text{m}$)^[3a] or on the flat surface of the SiO₂, which allow devices to be fabricated with $L = 40 \mu\text{m}$.^[3c] The promising nature of the molecular approach is demonstrated impressively by a functional 15-bit code generator consisting of more than 300 integrated SAMFETs.^[3b] A chemo-responsive monolayer transistor functionality was demonstrated by a monolayer of covalently bonded hexabenzocoronenes (HBCs) on a SiO₂ surface self-assembled in a tiny gap a few nanometers long in a pattern of SWCNTs, which provided the S/D contacts.^[3e] In situ self-assembly of a monolayer FET was observed by using ortho-hydroxyl-functionalized tetracene on AlO_x in 40 nm gaps between gold electrodes.^[3f] Functionalized poly- or oligothiophenes, self-assembled (via the PA anchor group) on ZnO surfaces, serve as active layers in hybrid solar cells and demonstrate that the concept of self-assembled functional device layers is a universal concept.^[3g]

New results approach the low voltage CMOS (complementary metal–oxide–semiconductor) ability of the SAMFET concept (Figure 2a–d). As p-type material a quaterthiophene C₂-4T-C₁₂-PA serves as a suitable π -system (Figure 2c). The ability to self-assemble and the low-voltage operation of the resulting SAM are implemented by an asymmetric substitution pattern with a *n*-dodecyl-phosphonic acid tail (C₁₂-PA), in which the C₁₂-chain contributes to a hybrid dielectric of about 5.3 nm thickness (C₁₂-PA ≈ 1.7 nm and AlO_x ≈ 3.6 nm). A C₆₀ derivative (Figure 2b) that is also linked to an *n*-alkyl phosphonic acid creates the *n*-type SAMFET. The corresponding SAMFETs operate in short-channel devices ($L < 1 \mu\text{m}$) but also in devices with channel lengths of up to 10 μm . The device fabrication method is fully comparable to the approaches used for flexible electronics. However, the rough surface of the Al/AlO_x pattern (root mean squared roughness ca. 1.5 nm) limits the device

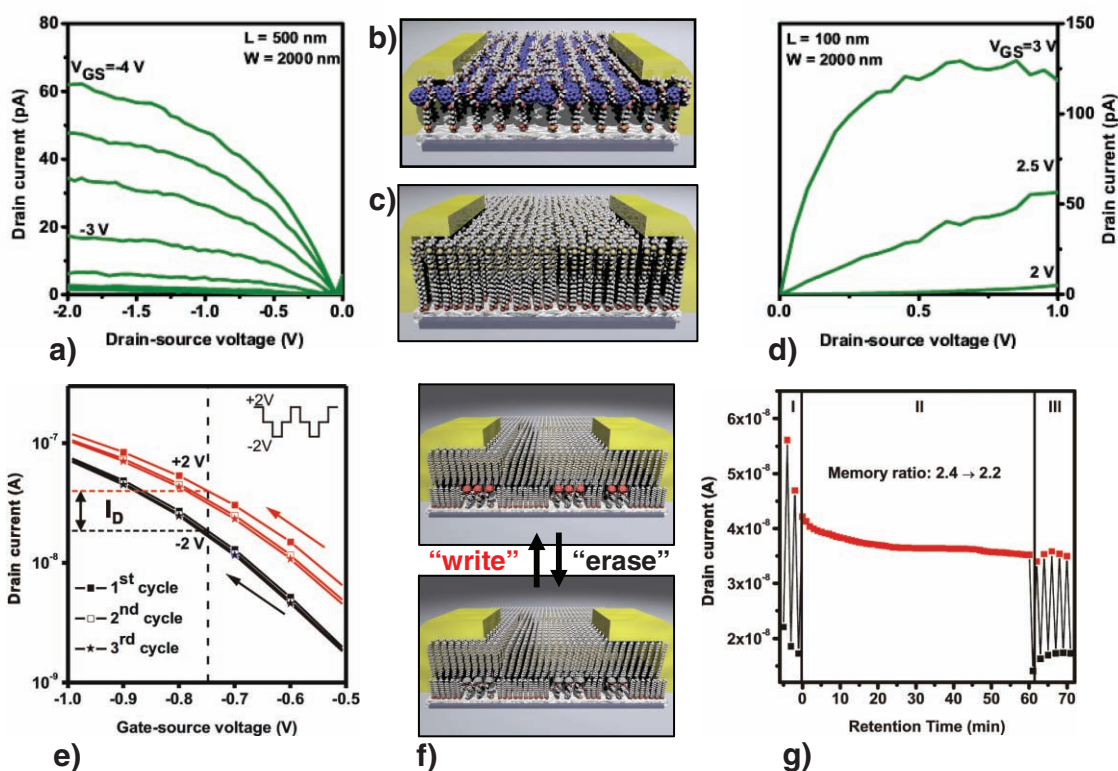
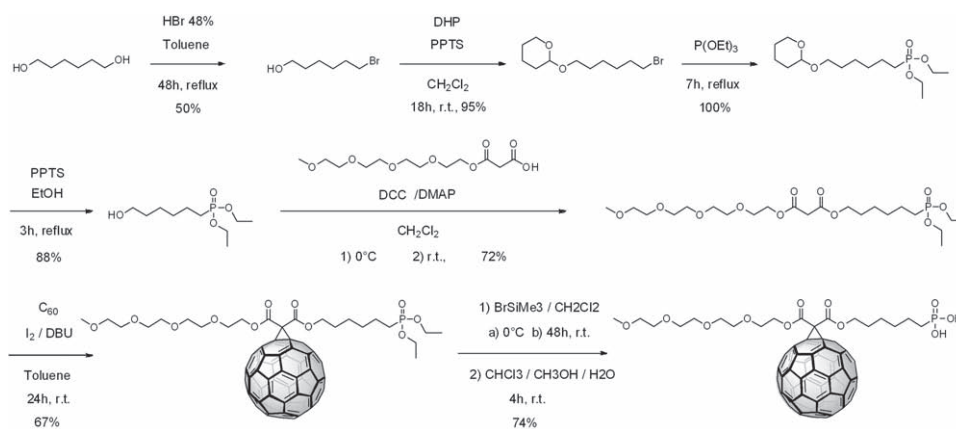


Figure 2. a) Output characteristics of a SAMFET with C₂-4T-C₁₂-PA active layer. b, c) Schematic sketches of SAMFET devices with glycol-C₆₀-C₆-PA (b) and C₂-4T-C₁₂-PA (c). d) Output characteristics of a SAMFET with glycol-C₆₀-C₆-PA active layer.^[3d] e) Capture of transfer characteristics of repeated program/read/erase/read operations of a device with C₆₀-C₁₈-PA-SAM. f) Schematic sketch of the two memory states and g) reversible switching behavior (regions I and III) and retention of the “on-state” (region II) of a memory TFT containing 1% C₆₀-C₁₈-PA.^[4b]

performance ($\mu \approx 10^{-4} \text{ cm V}^{-1} \text{ s}^{-1}$). Within the molecular structure of the C₆₀ derivative an additional oligo-glycol chain was implemented (glycol-C₆₀-C₆-PA) to provide solubility and to serve as at least a weak barrier on top of the SAM, allowing device operation in ambient air.^[3d] This means that the molecular design addresses four functionalities — i) selective self-assembly: PA anchor group; ii) part of the dielectric layer: *n*-alkyl chain; iii) *n*-type semiconductor: C₆₀; and iv) protection layer: glycol — in a SAM layer thickness of 2.5 nm. The SAMFET approach

clearly benefits from a reduced complexity in device fabrication, providing regio-selective deposition of several device layers with one molecular structure and in one step.

The synthetic approach for such *n*-type SAMFET materials is shown in **Scheme 1**. The PA termini connected to C₆₀ were used as anchoring units in SAM formation. Before binding to C₆₀ the PA unit was equipped with long alkyl chains. The next step was the conversion into malonates. These malonates containing the PA anchoring unit and insulating alkyl chain were



Scheme 1. Synthesis of tetraglycol-C₆₀-C₆-phosphonic acid.^[3d]

subsequently allowed to react with C_{60} by nucleophilic cyclopropanation. The reactions proceed under mild conditions and lead to easy-to-isolate and easy-to-separate monoadducts, which are stable at ambient conditions and can be handled and processed without any precautions. Such fullerene monoadducts still contain 58 π -electrons. As a consequence, most of the electronic properties of the parent C_{60} (60 π -electrons) are retained. A whole family of C_{60} -PA derivatives with various combinations of spacers and terminating side groups is accessible by this routine.^[3d,4b]

5. Mixed SAMs

So far, all applications of SAMs rely on the homogeneous assembly of one type of molecule or on layer-by-layer approaches, in which each individual layer also consists of one sort of molecule. A new research trend focuses on mixed SAMs (composed of different molecules; see Figure 1d) in devices.^[4a,b] Typically, solution processing and the same anchor chemistry enable full control of the SAM composition, which directly relates to the stoichiometric composition of the solution. This extends the possibilities of manipulation of device characteristics from “digital” (related to molecular structure) to “continuous” tuning (related to the stoichiometry of SAM composition). Zschieschang et al.^[4a] have demonstrated a concept in which they implemented fluorinated molecules (pentadecylfluorooctadecylphosphonic acid (FC_7 - HC_{11} -PA)) and *n*-octadecylphosphonic acid (HC_{18} -PA) as hydrocarbon molecules for pure and mixed SAM hybrid dielectrics in TFTs with pentacene and F_{16} CuPc (copper-hexadecafluoro-phthalocyanine) as the semiconductor. The threshold voltages could be shifted from -1.1 V for pentacene (pure H-PA) and 1.1 V for F_{16} CuPc (pure F-PA) to -0.5 V and 0.6 V (pentacene and F_{16} CuPc) in a 50/50 mol-% mixture of H-PA and F-PA. This leads to improved characteristics in complementary integrated inverters, namely increased signal gain to 430 with a 50/50 dielectric (compared to <100 for pure H- or F-SAM) and smaller supply voltages in complementary ring oscillators of only 1 V instead of 1.5 V and 2.5 V for pure H-SAM and F-SAM, respectively.^[4a] Another concept by Burkhardt et al.^[4b] used C_{60} -terminated octadecylphosphonic acids (C_{60} - C_{18} -PA) and *n*-octadecylphosphonic acid (HC_{18} -PA) in mixed hybrid dielectrics (AlO_x /SAM) in TFTs with α,α' -dihexylsextiophene (Hex-6T-Hex) as the semiconductor (Figure 2f). Depending on the concentration of C_{60} molecules within the SAM, a tunable shift in V_{TH} (from -0.88 V to $+0.76$ V for pure HC_{18} -PA and pure C_{60} - C_{18} -PA, respectively) and an increasing hysteresis during operation was obtained. The hysteresis is attributed to a charging of the C_{60} moieties and remains virtually constant over time (up to 6 h). Even when the supply voltage is removed. Depending on whether the mixed SAM-layer is charged or not, two distinguishable states in the TFTs are defined (Figure 2a,c) and the mixed SAM provides the characteristics of a non-volatile memory dielectric layer.^[4b] The second example indicates that mixed SAMs could open a new approach to creating new device features with simple methods.

In the two examples, the device characteristics do not scale linearly with the stoichiometric composition of the SAM, but are reproducible and with the option to tune device

parameters.^[4a,b] However, simultaneous self-assembly of different molecules induces a new fundamental question with regard to the SAM morphology and intermolecular arrangement of the molecules. While similar molecules tend to aggregate into discrete domains,^[4c] the arrangement of molecules that differ in the size of the head group (HC_{18} -PA and C_{60} - C_{18} -PA) occurs randomly.^[4b] A systematic study is needed to fully understand the self-assembly and the consequences for device characteristics.

6. SAM in More Highly Integrated Devices

One major concern related to SAMs, in particular to those which act as functional device layers, was the question of whether a single molecular layer is able to provide reliable performance. Secondly, the question of stable device operation with respect to mechanical stress, elevated temperatures, and chemical treatment appears critical.

The issue of reliable performance has been positively answered by several groups, who provided statistical evidence of SAM properties and used SAMs in integrated devices. Thereby, a remarkable complexity was achieved, including inverters, ring oscillators, code generators, and digital-to-analog converters with single-carrier approaches as well as with CMOS-like circuitry.^[2c,3b,5] Also the capability of reliable mechanical flexibility was demonstrated on polymer substrates, highly stretchable substrates, or even unconventional rough substrates such as banknotes.^[5] Recently, Seketani et al. have shown that SAM hybrid dielectrics can be fabricated in a stacked architecture in TFTs — creating a floating gate memory transistor operating at low supply and programming voltages (Figure 3a–d) — and can be combined with pressure-sensitive rubber sheets to form a flexible sensor array with a remarkable retention times of several hours.^[5e] That proves the high reliability and the possibility of using that technique for complex device structures with new application features. Even drastic bending conditions (bending radius of 0.1 mm) have no essential impact on the SAMs in TFT devices (setup, see Figure 3e) if the device is captured between two polymer sheets.^[5f] Integrated devices (complementary inverter and ring oscillator) operate up to a bending of 0.3 mm, which is essentially rolled-up (Figure 3f). Such TFTs were used to create ultra-flexible and stretchable pressure sensor arrays, in which the pressure or strain sensitivity is generated by a pressure-induced conductive pathway from a counter electrode through a pressure-sensitive rubber sheet, connected to the source electrode of a TFT with SAM dielectric (Figure 3g–i). This setup enables pressure detection with spatial resolution, relying on the virtually unchanged operation of the TFT array.

7. Conclusions

Molecular self-assembly is a powerful tool for creating reliable functional films in organic electronic devices with full control of the film thickness and, if necessary, with spatial resolution. Owing to the chemical diversity of accessible molecules, the different approaches in SAM composition (pure-, mixed-, and multilayer and hybrid systems), and simple processing, an

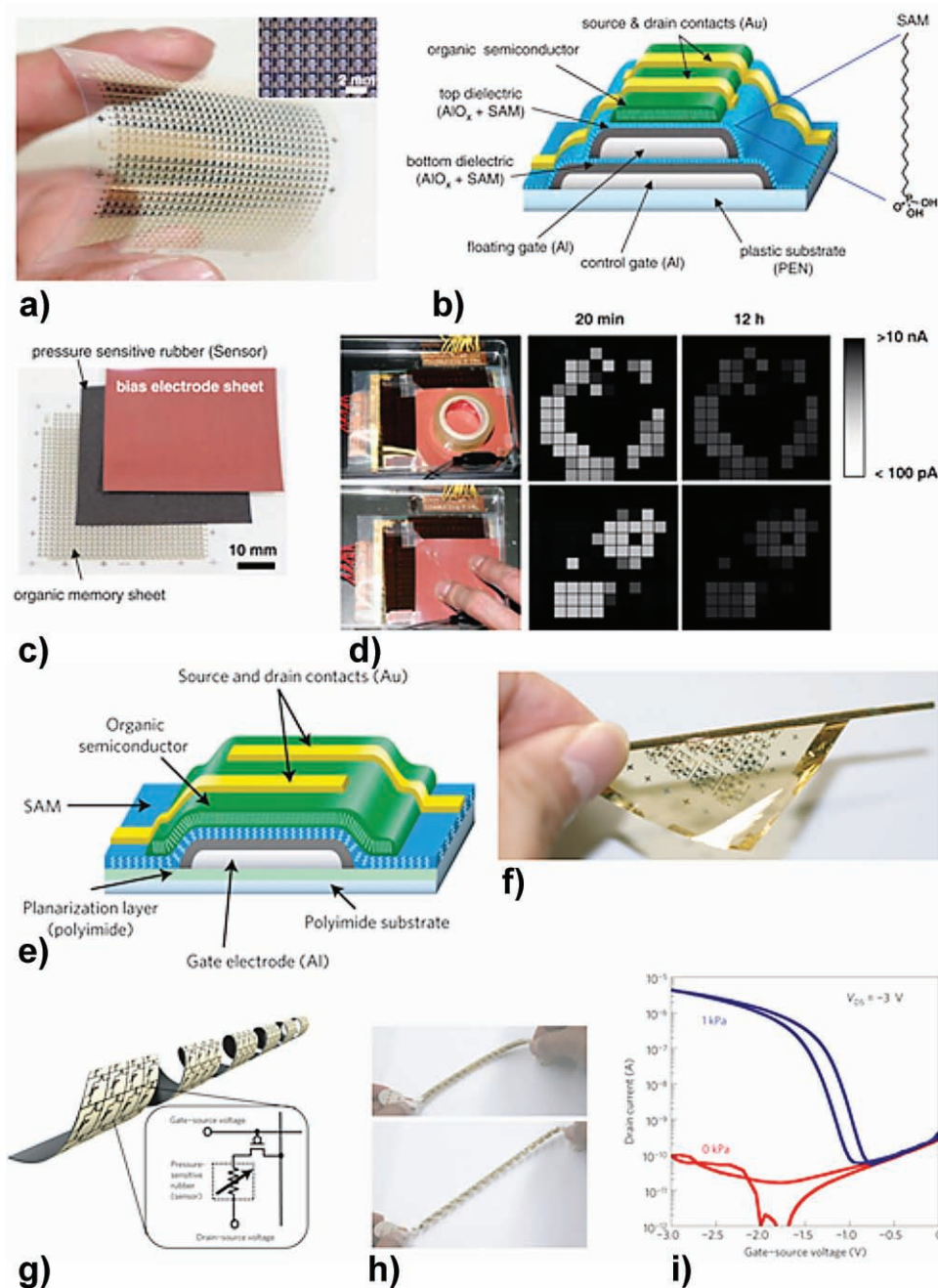


Figure 3. a) Photograph of an organic floating-gate transistor sheet comprising 26 by 26 memory cells. The inset shows a magnified image of the array. b) Schematic cross section of the floating-gate transistors. c) Photograph of the three individual sheets before lamination. Bottom, 125- μm -thick PEN sheet with 676 two-transistor (2T) memory cells; center, 500- μm -thick pressure-sensitive rubber sheet; top, 125- μm -thick PEN sheet with copper electrode. d) Demonstration of the sensor array. Reproduced with permission from [5e]. Copyright 2009 AAAS. e) Schematic cross section of the TFTs. f) Photograph of a polyimide substrate with functional organic TFTs and circuits wrapped around a cylinder with a radius of 300 μm . g) Circuit diagram of an ultraflexible active-matrix pressure-sensor array in the shape of a tightly wound helix. h) Photographs of a TFT array fabricated on a shape-memory polymer film (Nippon Mektron, Japan). i) Transfer characteristics of an individual sensor cell measured at two different pressures. Reproduced with permission from [5f]. Copyright 2010 Macmillan Publishers Ltd.

enormous construction kit is available to create functionality, combine functionality, and even integrate functionality in complex architectures. Thereby, new molecules with increased complexity, mixed layer approaches, and integrated devices are

the newest trends with enormous potential to achieve smart molecular scale electronics. The impressive “proof of concept” of these new device concepts outperforms the detailed knowledge of the intermolecular arrangement or SAM formation

steps at the molecular level and makes detailed investigation necessary.

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