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Edited by Mihai Irimia-Vladu, Eric D. Glowacki,
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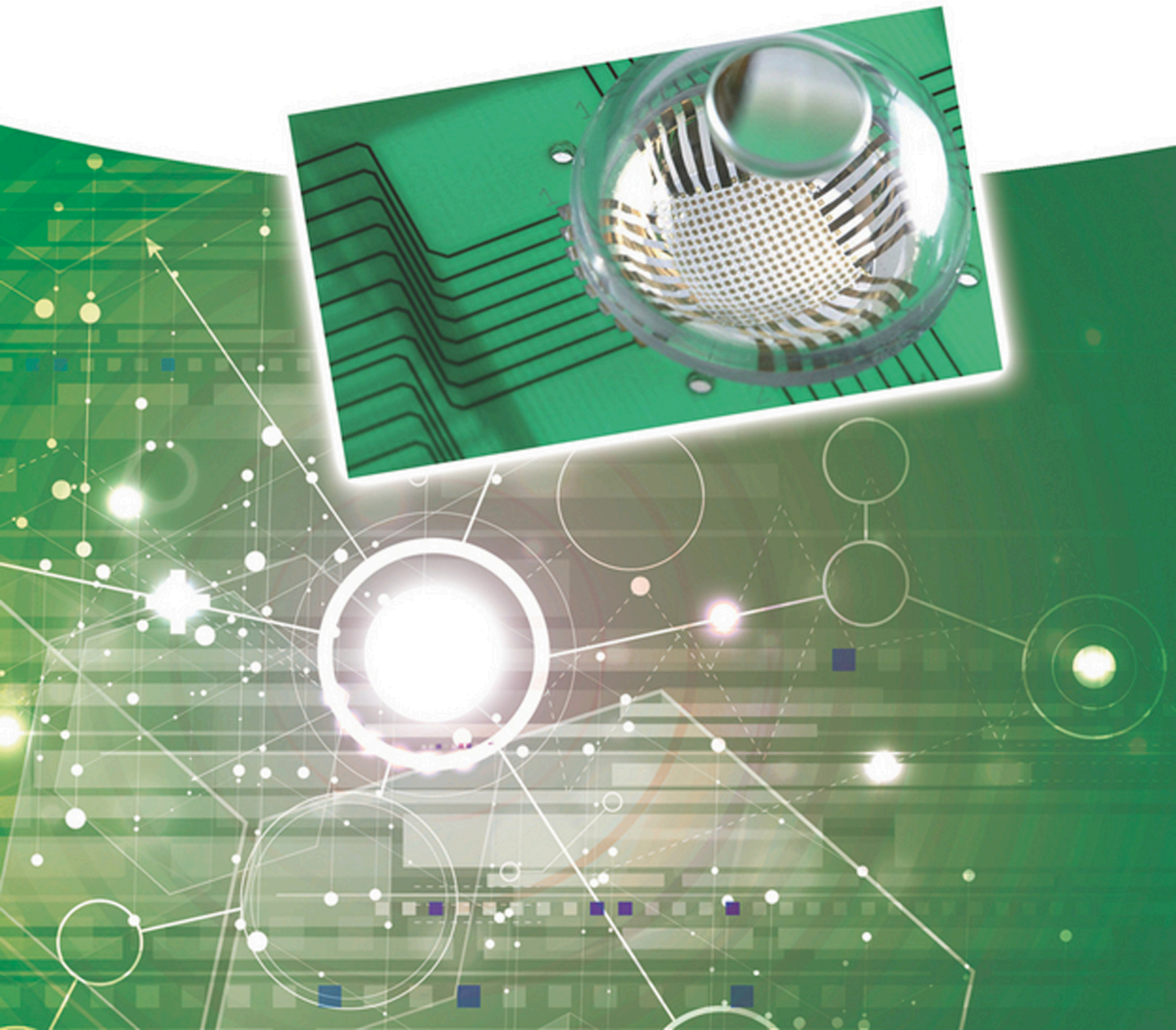

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Preface

Bioorganic electronics is rapidly growing, motivating the writing of this book as a commentary on the state of the art of the field. We are indebted to all contributors for their excellent chapters, which we hope the reader will find illuminating and informative as this exciting new field develops.

Bioelectronics has been a dream of cybernetics for quite some time. The pioneering work of Peter Fromherz (Max Planck Institute for Biochemistry, Germany) interfacing neurons with silicon circuits dates back several decades. Bioelectronics has been limited to silicon circuits for quite some time. Recently, the expansion of organic electronic devices has opened up a new avenue to realize this dream of interfacing biological systems with electronic circuits.

Organic conducting materials can speak the language of biological systems with their unique properties of hybrid ionic/electronic conduction, combined with electrochemical activity. Organic semiconductors, especially biocompatible semiconductors, display a list of properties important for the interfacing of biological systems with the electronic world. Their biocompatibility, nontoxicity, processability, and increasingly operational stability in aqueous media offer unique benefits inaccessible to their inorganic counterparts.

To make an interface with biosystems, electrical information must be transformed into ionic and protonic signals. Biosystems are often based on ionic charge transport and on signal transduction based on electrochemical systems, as opposed to the electronic world relying on electronic conduction of solid-state materials. In transforming signals from the electronic world to the bioworld, we need materials and systems such as transducers, which sustain electronic as well as ionic conduction. Organic electronic materials offer this possibility also because of their chemical tenability. As several chapters in this book will show, the derivatization of organic semiconductors enables unique electronic device functions. Therefore, we envision that the future of cybernetics might be using more and more organic/bio-organic semiconductors (Figure 1).

On the other hand, we believe it is highly useful to stress the concept of *green* electronics to sustain a sound and healthy environment. We already have today a severe problem with electronic waste in our world. Humanity is currently not able to create a sustainable cycle for the production, use, and end-of-life of electronic gadgets and instruments. Often such products are disposed in ordinary garbage dumps, polluting our environment and wasting highly valuable materials as well (Figure 2).

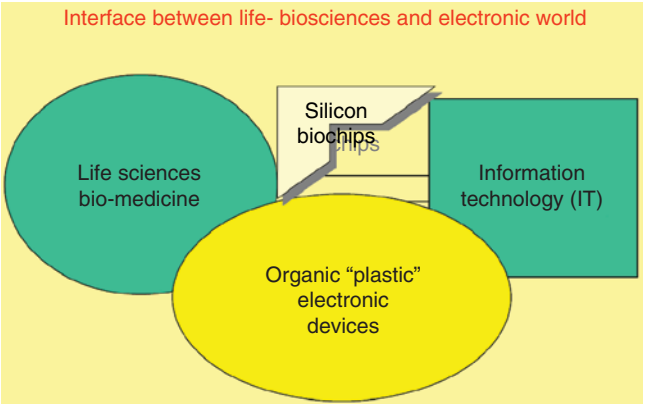

Figure 1 Future cybernetics as an important mission of organic electronics.

Figure 2 A child at an electronic dumping ground in China sits among a pile of wires and e-waste. The e-waste is exported from all over the world to less developed countries, mostly in Asia and Africa, where children often handle e-waste containing many hazardous chemicals. (Image reproduced with permission from Greenpeace International.)

Akio Morita, the founding chairman of SONY once stated:

"We are moving from consumer electronics to consumable electronics."

Upon this premise we clearly see that electronic waste is and will be an increasing problem. By using plastic materials for organic solar cells, organic light-emitting diodes, and so on, we will face a mounting problem of plastic waste, already polluting our oceans. Polyolefins and commodity plastics are often not biodegradable and impose a problem when they end up in the biosphere.

These problems may be mitigated with the use of biodegradable and nontoxic materials. Several chapters in this book cover a creative repurposing of mass-produced materials for *green* electronics, such as paper, DNA, diatomous silica, and various bioresorbable materials. These materials can be tailored to be biodegradable by the end of their life cycle, or to degrade transiently *in vivo* for medical applications.

Such ideas and many more propositions are found in the chapters of this book. Of course the editors do not claim completeness of coverage of this topic with this book; the field is vast and fortunately growing rapidly. We do believe that several core concepts are introduced and these concepts will retain their relevance in future bioelectronic technologies. We sincerely hope that in some years many such books will be available, carrying the flag further in different territories of science. We wish all colleagues embarking on new science in this field the best of luck.

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1

Emerging "Green" Materials and Technologies for Electronics

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1.1 Introduction to "Green" Materials for Electronics

We are currently witnessing an evolution of technologies blurring the lines between the physical, digital, and biological spheres. Electronics become highly flexible and even mechanically stretchable, with applications ranging from wearable consumer electronics to mobile health, sports, and well-being. The materials aspects of flexible and stretchable electronics is covered in depth by many pioneers in the field, summarizing also the latest developments spanning from stretchable interconnects to the level of highly sophisticated electronic skin [1–5]. A wide class of materials is available in thin film forms, ranging from dielectrics and semiconductors to metals, as well as a cornucopia of industrially relevant processing methods. Initial attempts toward biocompatible electronics paved the way toward epidermal [6] and implantable electronics [7–9]. Sustainable use of material resources is a major concern of our society, challenging research with the ever-growing amount of electronic waste, estimated to be 41.8 million metric tons (Mt) at the end of 2014 and forecasted to reach 50 million Mt by 2018 [10].

Inspiration from nature led to the first approaches to biodegradable forms of electronics, finally culminating in the development of transient electronics that simply degrades after service life [11]. The state of the art in "green" electronics has been summarized in a recent review, covering degradable substrates and materials for encapsulation, as well as dielectrics, semiconductors, and metals for basic electronic circuit elements [12]. In this chapter we will provide a brief overview on "green" materials for degradable circuit boards and organic electronics, including the latest developments in the field. We first summarize

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the use of paper, followed by a discussion of natural and nature inspired materials, including DNA and nucleobases; silk; saccharides; Aloe Vera, natural waxes, and gums; cellulose and its derivatives; resins; proteins, peptides, and amino acids; and finally natural and nature-inspired semiconductors for biodegradable and biocompatible electronics. We expect that in the future we will be as comfortable with highly flexible and degradable forms of electronics, embedded everywhere, in textiles, on skin, and even within our body as we are now familiar with smartphones and tablet computers.

1.2 Paper

More than 2000 years ago the Chinese inventive genius brought to light what is to date of incommensurable importance for humanity: paper, a natural-origin and sustainable (renewable and degradable) material. Good tunable physical properties, such as transparency or roughness, make paper desirable for large-area products. Paper wins over other flexible substrate materials owing to its low cost (below 0.1 USD m^{-2}), high flexibility, and the possibility for large-scale roll-to-roll manufacturing with speeds of processing exceeding 25 m s^{-1} [13]. When the cultivation of wood, the basic material for paper, is executed environmentally sustainably and when recycled paper is used in the fabrication process, paper outrivals most candidates for substrates in biodegradable devices. Apart from its classic usages for packaging, information storage, and as support for displays, paper recently developed into a substrate for a wide variety of unconventional electronics. Paper electronics is continuously drawing attention in the scientific community and is highlighted in this book extensively in Chapter 6 by Martti Toivakka *et al.* for a plethora of applications. In the following, we will only briefly present the usage of paper as substrate and dielectric for basic electronic circuits. Martins *et al.* have utilized, for example, both the above-mentioned assets of paper in a low power electronic Complementary Metal-Oxide-Semiconductor (CMOS) inverter circuit layered on a flexible and recyclable fiber-based paper substrate. The paper gate dielectric offers a large capacitance per area at low frequencies because of its fiber-based foam-like structure. Figure 1.1a displays an image of a CMOS inverter on paper, tested under different supply voltages. Figure 1.1b shows the voltage transfer characteristics (*VTC*s) of the inverters, which are used to extract the high and low states, associated with the input and output voltages. Gain and leakage current are extracted from Figure 1.1c [14]. Although the reported results are not impressive in terms of CMOS performance, the use of paper for a dual function of substrate and dielectric is highly promising since it enables layering of various semiconductor structures (dielectrics and semiconductors). The demonstration opens the door for implementing paper for a plethora of applications that can be broadly grouped under the umbrella of "green" electronics (memory elements and integrated systems, smart labels, tags, sensors, and electrochromic paper displays, to name a few).

The rough surface of paper, combined with its high absorbance tendency for various liquids, makes very challenging the processing of solution-based active layers on top of it. Pettersson *et al.* eliminated the problem of semiconductor absorption into the paper substrate by using a mixture containing a semiconductor

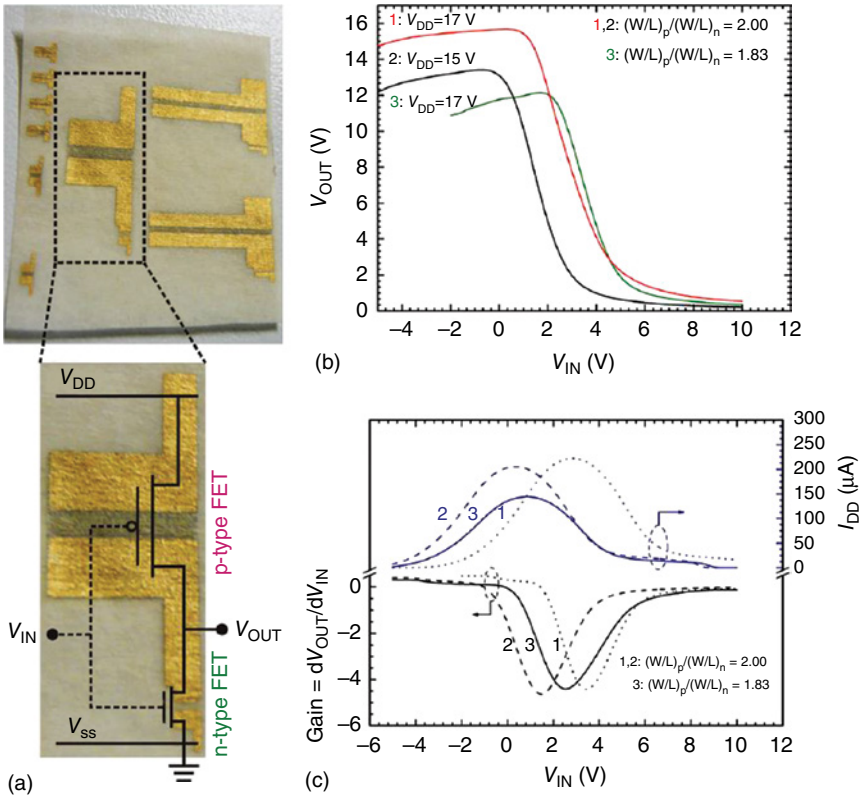


Figure 1.1 The potential of paper for the fabrication of future CMOS architectures: (a) photograph of a low-power electronic CMOS inverter circuit on paper; (b) the voltage transfer characteristics of the CMOS inverters; and (c) the gain, dV_{out}/dV_{in}, and the leakage current, I_{DD}. (Martins *et al*. 2011 [14]. Reproduced with permission of John Wiley and Sons.)

and a biodegradable polymer insulator [15]. In this compound, spontaneous phase separation occurs, and a thin semiconducting layer is formed on top (Figure 1.2Aa). Owing to this preparation step, the sensitive semiconductor was separated from the paper substrate. Importantly, the rough surface of paper does not play an important role anymore, in that it does not transpose its unevenness through the dielectric and to the dielectric–semiconductor interface where the charge transport occurs. Another aspect of utmost importance is the stability of devices fabricated on paper. Pettersson *et al*. examined the bias–stress stability and the shelf life of transistors on paper [16]. These transistors were connected in advanced circuits, including NOR gates and D-latches. Stabilities of up to 3 weeks were observed, currently limiting the usage of such paper electronic devices to short-term applications only. To prove the operation principle, a logic NOR-gate was fabricated with two transistors and one 5.6 MΩ resistor. For NOR gates, a high output (i.e., value of 1) results if both the inputs to the gate are low (i.e., both display a value of 0). Figure 1.2B shows the output of such logic circuit device with a low operating voltage and fast switching of the states, from one state to the other [16].

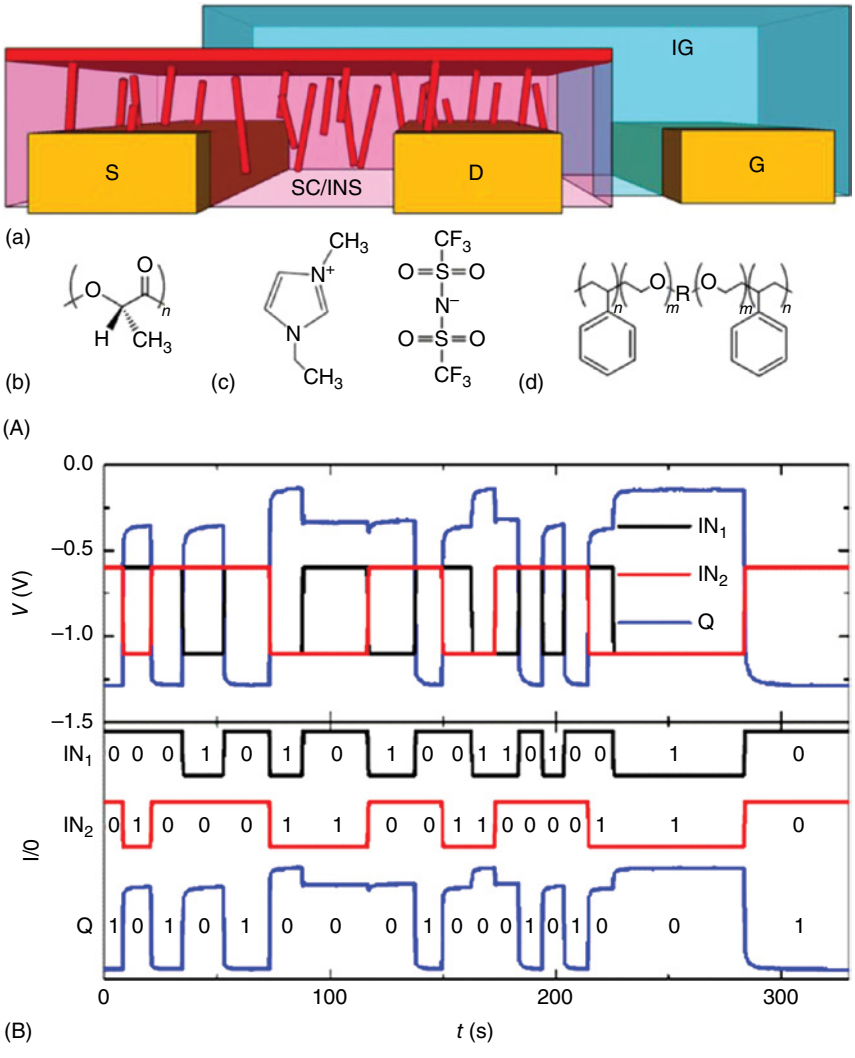


Figure 1.2 (A) (a) Schematic of the OFET structure containing the gate (G), source (S), and drain (D) electrodes, the ion gel (*IG*,) and the self-separating semiconductor insulator blend (SC/INS); (b) the chemical structure of the poly(L-lactic acid) (*PLLA*); (c) the chemical structure of the ion gel used, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM:TFSI); and (d) the chemical structure of the triblock copolymer, PS:PEO:PS (7 wt%), used as a gelling agent for the ion gel. (Pettersson *et al*. 2014 [15]. Reproduced with permission of Cambridge University Press.). (B) Output data of the NOR-gate with a supply voltage, V_{DD}, of −1.3 V. The raw signals are superimposed in the top graph and presented deconvoluted in the bottom graph. (Pettersson *et al*. 2015 [16]. Reproduced with permission of John Wiley and Sons.)

Paper, although a challenging material for device preparation, opens the door to low-cost disposable electronics. Electronic devices fabricated on paper will need also a power supply, and for such purpose paper-based photovoltaics could be a perfect complement. Paper appears to be an ideal support material for photovoltaic cells,

being ~1000 times less expensive than glass and ~100 times less expensive than common plastics. Barr *et al.* demonstrated the potential of unmodified paper for photovoltaics fabrication [17]. The paper photovoltaic arrays reported by the group generated impressive performance: an open circuit voltage approaching 50 V and a current of ~10 μA capable of powering electronic displays under ambient indoor lighting for at least 6000 h of uninterrupted power supply. Moreover, the photovoltaic arrays could be tortuously flexed and folded without loss of function. In 2014 Leonat *et al.* showed that nearly doubling the Power Conversion Efficiency (PCE) (i.e., reaching efficiencies of 4%) compared to the one reported in reference [17] for an individual polymer-based photovoltaic cell on paper is possible [18]. Figure 1.3a displays the component materials used in the fabrication process of the organic solar cell on a double-side coated image printer paper that is displayed in Figure 1.3b.

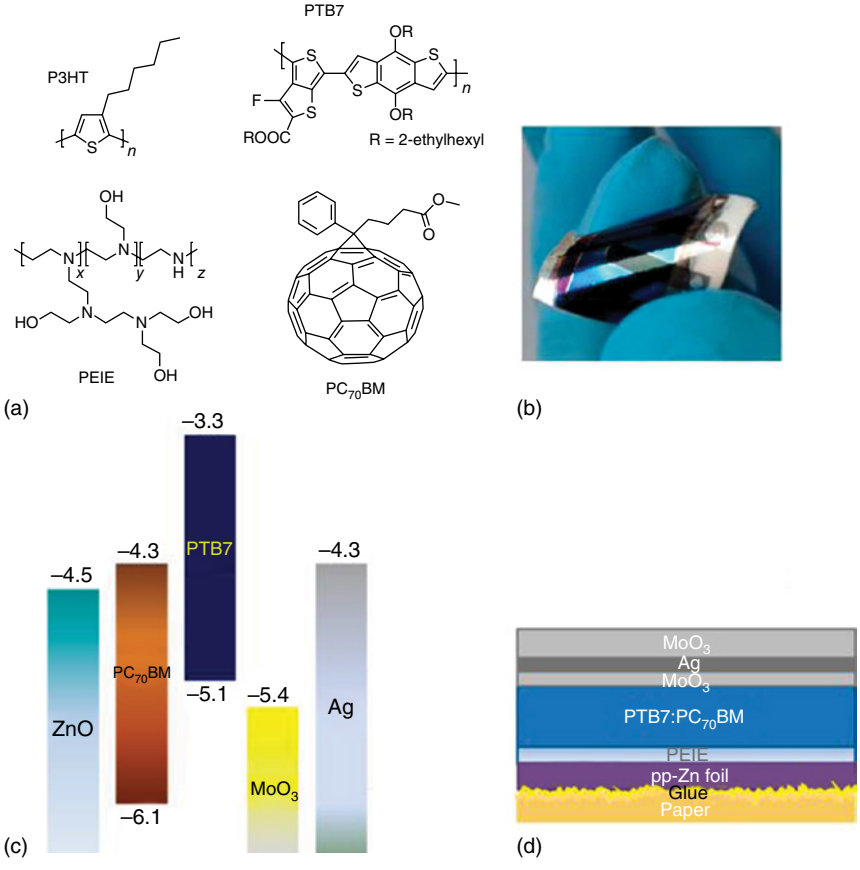
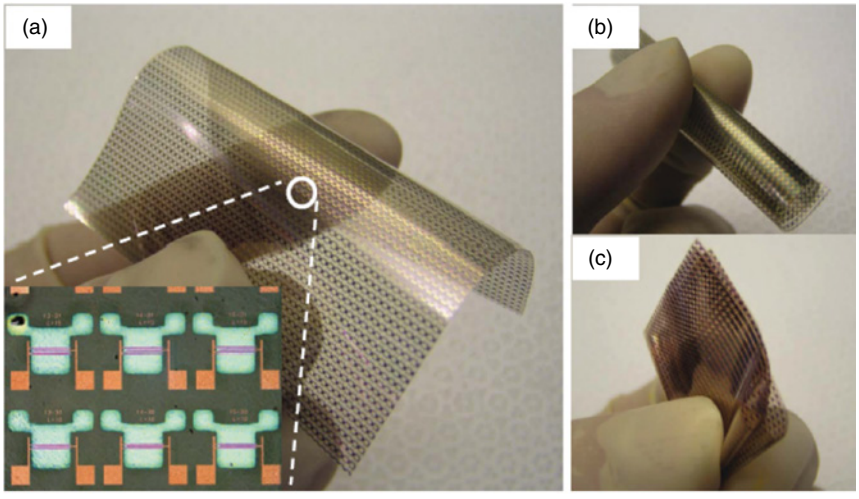


Figure 1.3 (a) Chemicals employed in bulk fabrication of heterojunction solar cell devices: standard P3HT and novel PTB7 polymers as electron donors; $PC_{70}BM$ as electron acceptor; polyethylenimine (*PEIE*) deposited in a thin layer (10 nm) coating to improve the work function and injection of ZnO back electrode; (b) photograph of a 4% efficient organic solar cell on a flexible paper support; (c) energetic levels of the photovoltaic layers; (d) schematic of the fabricated device showing the sequence of the layers. (Leonat *et al.* 2014 [18]. Reproduced with permission of American Chemical Society.)



(A)

	1	2	3	4	5	6	7	8	9	10	Mobility	No. of TFTs
A	0.24	0.19	0.30	0.25	0.21	0.26	0.22	0.24	0.04	0.13	0.00 – 0.04	7
B	0.23	0.00	0.29	0.21	0.28	0.35	0.40	0.14	0.19	0.20	0.05 – 0.09	5
C	0.34	0.36	0.26	0.24	0.36	0.48	0.26	0.44	0.21	0.26	0.10 – 0.14	7
D	0.16	0.29	0.22	0.16	0.01	0.00	0.40	0.35	0.06	0.39	0.15 – 0.19	12
E	0.14	0.35	0.45	0.43	0.43	0.28	0.02	0.34	0.19	0.23	0.20 – 0.24	19
F	0.16	0.20	0.22	0.38	0.36	0.30	0.02	0.34	0.05	0.19	0.25 – 0.29	16
G	0.16	0.36	0.11	0.27	0.40	0.33	0.57	0.23	0.13	0.38	0.30 – 0.34	10
H	0.16	0.47	0.12	0.24	0.18	0.24	0.38	0.04	0.29	0.23	0.35 – 0.39	12
I	0.27	0.34	0.24	0.06	0.14	0.27	0.17	0.05	0.56	0.17	0.40 – 0.44	7
J	0.34	0.33	0.26	0.44	0.23	0.32	0.37	0.07	0.28	0.25	0.45 – 0.49	3
											0.50 – 0.54	0
											0.55 – 0.59	2
												Σ 100

(B)

Figure 1.4 (A) (a) Photograph and a magnified image by optical microscopy of transparent, nanopaper-based OTFT array. Photographs revealing the (b) bending and (c) folding deformation modes endured by the substrate. (Fujisaki *et al*. 2014 [19]. Reproduced with permission of John Wiley and Sons.) (B) Field-effect mobility map of the transistor array on 5€ paper banknote with an area of $10 \times 8\,mm^2$ showing the distribution of the field-effect mobility. (Zschieschang *et al*. 2011 [20]. Reproduced with permission of John Wiley and Sons.)

The coating is based on a zinc metalized polypropylene thin film, where propylene serves as smoothener of the rough paper surface and prevents capillary penetration of the solution-processed active layers into the paper substrate, while zinc is employed as the metallic electrode of the device. Energy band diagrams of the components and the layered sketch of the device are presented in Figure 1.3c,d respectively [18].

A next step will be the realization of truly 3D-shaped paper electronics; in this respect Kirigami techniques seem promising to make paper not only flexible but even stretchable. Highly flexible, sustainable optoelectronics may soon become a reality with the aid of highly transparent paper. Cellulose nanopaper (made from nano-sized cellulose fibers) was selected as substrate for flexible electronics, as reported by Fujisaki *et al.* [19] Initial work employed a 20 µm thin transparent paper, made from native wood cellulose nanofibers only, as substrate for fabrication of high-mobility organic thin film transistor (TFT) arrays. Figure 1.4Aa depicts a photograph and an optical microscopic image of a 20 µm thin transparent nanopaper-based OTFT array. Figure 1.4Ab,c demonstrate the amenability of the substrate material to withstand torturous deformation, in a similar way to conventional paper.

OTFT arrays might also be a good option for anti-counterfeiting and tracking feature applications, especially when printed directly on banknotes. Zschieschang *et al.* demonstrated the fabrication of complex circuits with high yield and reproducibility directly on the rough surface of paper bills [20]. Such circuits could form advanced electronic safety features for counterfeit protection (Figure 1.4B). In a recent report Kim and coworkers demonstrated for the first time one-dimensional photonic nanocavities on paper after their transfer printing with the aid of a micro-sized stamp [21].The nanocavity exhibits lasing (Figure 1.5) and displays a wavelength shift dependent on the amount of hydration of the paper substrate, proving also its amenability to function as a sensor. Although the *Q*-factor is

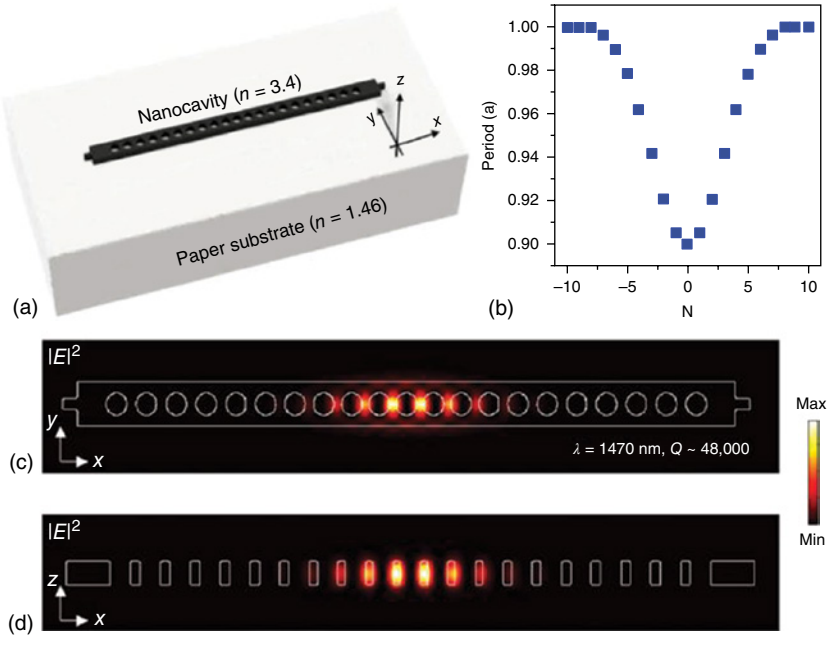


Figure 1.5 (a) Schematic of a semiconductor photonic nanocavity laser deposited via transfer printing on a paper substrate; (b) the Gaussian-modulated period of hole-to-hole distances along the *x*-axis from 0.9a to 1.0a. (c) The electric field intensity of the photonic crystal on the *x*–*y* plane and (d) the electric field intensity of the photonic crystal on the *x*–*z* plane. (Kim *et al.* 2016 [21]. Reproduced with permission of John Wiley and Sons.)

reduced by a factor of 10 when the paper substrate is introduced as support for the free-standing nanocavity crystal, the lasing threshold remains low, at ~0.2 mW. When employing the communication wavelength of 1.55 μm, the paper substrate provides a sufficiently high *Q*-factor for lasing, potentially paving a way for telecommunication applications. The selected research examples discussed here serve to illustrate the huge potential of paper for future development of sustainable electronics and photonic devices.

1.3 DNA and Nucleobases

In 1953, Watson and Crick published the helical structure of deoxyribonucleic acid, better known as *DNA* [22]. This investigation led to a better understanding of the main building block of every living organism on Earth and its genetic code transmittance responsible for growth, development, functioning, and reproduction. The long fibrous DNA molecule consists of a very long backbone chain formed by repeated units of a sugar group (deoxyribose) and a phosphate group alternately bonded to nucleobase molecules (the purines adenine and guanine, and the pyrimidines cytosine and thymine). Although the DNA-based research represented from its inception the bread and butter of genomics [23], the molecule stirred increasing interest over the past decade as a material for organic electronics, in the intention to bridge functional electronics with living organisms. Yumusak *et al.* demonstrated a bio-organic field-effect transistor (*BioOFET*) based on a cross-linked DNA gate dielectric, purified from salmon waste [24]. DNA is soluble only in aqueous solutions, which makes implementation of standard processing techniques from organic solvents difficult. The authors engineered a DNA–lipid complex that became water insoluble and processible in high quality films from organic solvents using standard device fabrication techniques such as spin coating. Steckl *et al.* paved the way for using DNA in organic light-emitting diodes (*OLED*s) and emphasized the potential of DNA as an inexpensive and biodegradable source material for the development of optical waveguides and laser structures [25, 26]. Thin films of DNA incorporated into the fluorescent emitting materials for OLEDs can increase the brightness of the respective devices by one order of magnitude compared to OLEDs produced from standard materials. The authors found that the DNA layer behaves as a highly efficient electron-blocking layer (*EBL*) while not hampering hole transport. Therefore, the thin DNA layer enhances the probability of exciton formation and eventually of photon emission in fluorescent OLEDs decorated with specific fluorophores (i.e., standard AlQ3 for green and NPB for blue emission respectively) as visualized in Figure 1.6a [27]. When DNA-surfactant thin films are incorporated in phosphorescent OLEDs, the brightness and efficiency of the DNA-based devices outperforms their phosphorescent counterparts, as revealed in Figure 1.6b.

DNA capping layers also enhance charge injection in OFETs, as demonstrated by Zhang *et al.* [28]. In their work, DNA works as an interlayer for n-type and ambipolar semiconductor OFETs fabrication with gold as top source and drain electrodes. The DNA layer in the device, schematically shown in Figure 1.7Aa, allows for the injection of both charge carriers. The OFET was prepared either

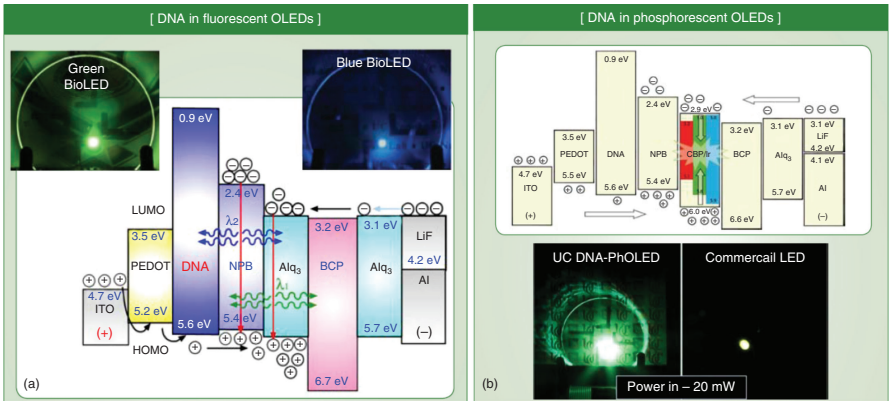
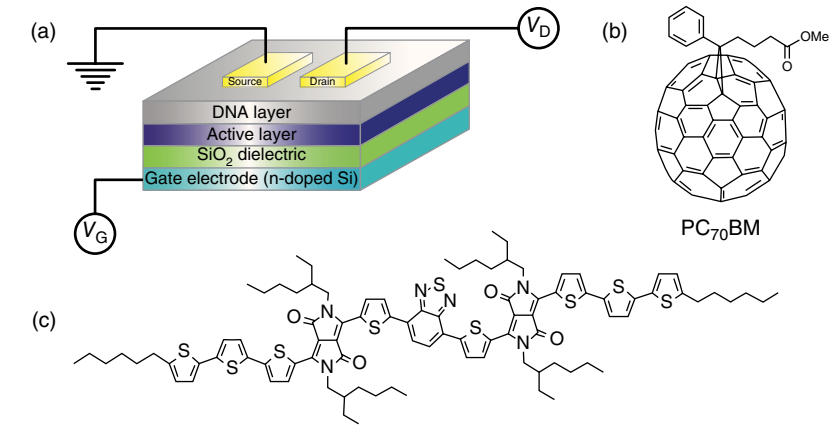


Figure 1.6 (a) Fluorescent OLEDs with DNA surfactant as electron-blocking layer employing AlQ3 fluorophore for green emission and NPB for blue emission. The bottom schematic displays the energy diagram of the layered structure; (b) DNA surfactant employed in the fabrication of phosphorescent OLEDs: the energy diagrams (top) of the layered structure, and the comparison of DNA-based OLED with a commercially available phosphorescent LED, with both devices biased at 20 mW (bottom). (Steckl *et al*. 2011 [27]. Reproduced with permission of Optics & Photonics News.)



(A)

	μ_{lin} (*e*) ($cm^2\ V^{-1}\ s^{-1}$)	μ_{sat} (*e*) ($cm^2\ V^{-1}\ s^{-1}$)	μ_{sat} (*h*) ($cm^2\ V^{-1}\ s^{-1}$)	V_{th} (V)[a]
$PC_{70}BM$	7.5×10^{-3}	9×10^{-3}	N/A	16
$PC_{70}BM$/DNA	1.7×10^{-2}	1.6×10^{-2}	N/A	10
BTDPP2	4.8×10^{-4}	4.4×10^{-3}	6×10^{-3}	12
BTDPP2/DNA	2.3×10^{-3}	1.1×10^{-2}	2.1×10^{-2}	6.5

(B) [a] V_{th} is determined from the linear regime under electron accumulation mode.

Figure 1.7 (A) (a) Schematic of the device structure with DNA used a charge injection layer and (b–c) chemical structure of the semiconductors employed. (Zhang *et al*. 2012 [28]. Reproduced with permission of John Wiley and Sons.) (B) Device parameters of OFETs fabricated using $PC_{70}BM$, $PC_{70}BM$/DNA, BTDPP2, and BTDPP2/DNA.

with an n-type semiconductor material, [6,6]-phenyl-C_{71}-butyric acid methyl ester($PC_{70}BM$) (with the structure depicted in Figure 1.7Ab) and 4,7-bis{2-[2,5-bis(2-ethylhexyl)-3-(5-hexyl-2,2′:5′,2″-terthiophene-5″-yl)-pyrrolo[3,4-*c*]pyrrolo-1,4-dione-6-yl]-thiophene-5-yl}-2,1,3-benzothiadiazole (BTDPP2) (shown in Figure 1.7Ac) or with an ambipolar semiconductor, diketopyrrolopyrrole (*DPP*). The fabricated OFETs having DNA as injection layer showed an increase in field-effect mobility of up to one order of magnitude as compared to the samples that have no such interlayer (see Figure 1.7B).

Far easier to process than DNA are its constituent nucleobases that are widely available in crystalline powder form; they can be used without purification, or alternatively can be scrupulously purified to a desired extent via the train sublimation method. AFM surface investigations of vacuum-sublimed thin films deposited on glass substrates demonstrated a root mean square (*rms*) roughness of ~3 nm for guanine, ~14.5 nm for adenine, ~24 nm for cytosine, and ~65 nm for thymine [29]. The authors showed that ultrathin layers of natural adenine, guanine, thymine, and cytosine can be used as stand-alone dielectric or in combination with one another in alternating layers.