

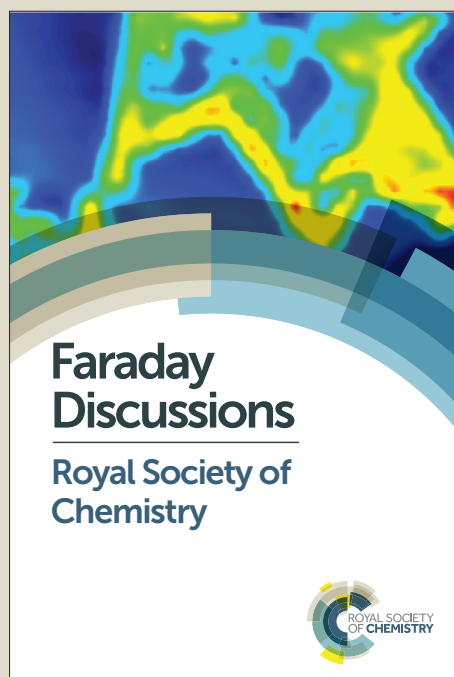
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# Organic electronics: an organic materials perspective

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This article is intended to provide a background to the Faraday Discussion 174: "Organic Photonics and Electronics" and will consist of a chronological, subjective review of organic electronics. Starting with "ancient history" (1888) and history (1950 - present), the article (talk) will take us to the present. The principal developments involved the processes of charge carrier generation and charge transport in molecular solids. Starting with insulators (photoconductors) moving to metals, to semiconductors and ending with the most popular semiconductor devices, such as, organic light-emitting diodes (OLEDs), organic field effect transistors (OFETs) and organic photovoltaics (OPVs). The presentation will be from an organic chemistry/materials point of view.

## 1 Introduction

### 1.1 Why organic electronics?

The first question, of course, is whether one can fabricate organic devices that possess electronic and other materials properties analogous to, rivaling, or even surpassing those of traditional inorganic solids. Conventionally, most organic solids are lighter, more flexible and more elastic than their inorganic counterparts. For e.g., in terms of mechanical properties, one can compare a Kevlar® fiber to a thin steel wire, where the former is stronger than the latter, yet is lighter and more flexible. At the heart of organic solids is the element carbon that distinguishes itself from the rest of the periodic table by producing long chains and rings involving double bonding with itself as well as nitrogen, oxygen, boron, sulfur and phosphorus. Carbon also forms stable triple bonds with itself and nitrogen. It stood (and stands) to reason, then, that one should be able to take advantage of the properties of carbon compounds but add to the list all the exciting possibilities of transporting charges, a property that until relatively recently, was associated only with traditional semiconductors.

### 1.2 History: organic metals and superconductors

For this article, ancient history is defined as events in physics and chemistry of organic solids that predate the Rutherford model of the atom (1907). At first, scientists in the XIX century concerned themselves with achieving (observing) electrical conductivity in organic solids. According to Gutmann and Lyons (G&L),<sup>1</sup> who quoted Vartanian,<sup>2</sup> who, in turn, claimed that the first paper dedicated to the observation of a photovoltage by an organic dye was by the Russian N. Stoletov in 1888. In Western Europe, according to G&L, Pochettino was the first to observe

photoconductivity in anthracene in 1906.<sup>3</sup> Between 1948<sup>4</sup> and 1953, dark resistivities of organic solids were found to be on the order of  $10^{11} - 10^{18} \Omega/\text{cm}$ .

A very important event took place in 1951, when Inokuchi and his group<sup>5</sup> reported a resistivity of  $10^{-1}$  for an organic charge-transfer complex. This was followed by the DuPont work on charge-transfer salts of TCNQ<sup>6</sup> with resistivities on the order of  $10^{-2} \text{ W/cm}$ . In the 1970's, with the advent of TTF TCNQ, the first organic solids exhibiting metallic conductivity were developed.<sup>7</sup> Research on these compounds quickly led to the discovery of organic superconductors.<sup>8</sup> At first the very low transition temperatures were achievable only under substantial pressure (25 kBar) but eventually the transition temperature was raised ca 13 K at atmospheric pressure<sup>8</sup> and ultimately 40 K for a fullerene salt.<sup>9</sup> A rather high value, especially considering that before the appearance of the high  $T_c$  cuprate superconductors, the highest ever observed  $T_c$  was only in the range of 22 -23 K. In summary, before the end of the XX century, not only were charges generated in organic solids but they could also be transported with minimal resistance (metallic) to zero resistance (superconducting). The lessons learned from these developments were that the requirements for charge generation and transport were  $\pi$ -bonded carbon compounds containing sulfur and nitrogen. Further, these molecules either readily donated electrons (donors, D) to molecules that would easily accept them (acceptors, A). These D-A solids formed stacks of planar molecules, where the stacks consisted of like molecules; i.e., segregated D and A stacks. In addition, the charge carriers in D-A ensembles delocalized preferentially along stacks, rather than between stacks. Finally, the stacks needed to be partially charged; i.e., carrying approximately one charge (+ or -) for every two molecules within a stack.

### 1.3 History: organic semiconductors

Whereas metals exhibit a non-activated conductivity, that is, their conductivity increases with decreasing temperature, semiconductors show activated conductivity. The charge carriers in the former are in a partially filled conduction band (CB), whereas in semiconductors, charge carriers are either thermo- or photo- excited from the filled valence band (VB) to the empty CB. In the case of organic semiconductors, it is relatively easy to remove electrons from the valence band of a D or add electrons to the empty conduction band of A. These processes have a dramatic effect on the electronic properties of the semiconductor. Thus, electron removal from D, accompanied by introduction of a counter anion to the resulting hole is considered *p*-doping and addition of an electron to A with addition of a counter cation to the electron is labeled *n*-doping. The VB of organic semiconductors is the  $\pi$  molecular orbital (MO) and the CB is the  $\pi^*$  MO. The semiconductor gap of organic semiconductors can be relatively easily engineered to vary from larger than 3 eV to ca 0.5 eV. This translates to interband light absorption wavelengths ranging from the UV to the NIR.

## 2. Classes of organic semiconductors

### 2.1 Small molecules

The most popular family of small molecule semiconductors are the polycyclic aromatic hydrocarbons and, of these, pentacene and some of its derivatives are the most studied in terms of device applications. Pentacene has a bandgap of 2.2 eV. It

is a *p*-type semiconductor with a hole-mobility slightly higher than that of amorphous silicon, on the order of 5 cm<sup>2</sup>/Vsec.<sup>10</sup> Many dozens of organic  $\pi$ -bonded molecules have been examined in OFETs and a few of these have made it into J. Anthony's review.<sup>8</sup> These molecules contain sulfur as well as nitrogen. The overwhelming majority are *p*-type semiconductors with relatively low conductivities (10<sup>-12</sup> – 10<sup>-4</sup> S/cm), particularly, when compared to organic metals (10<sup>2</sup> – 10<sup>3</sup> S/cm). There are considerably fewer *n*-type semiconductor molecules. The salient examples are the acene imides such as naphthalene tetracarboxylic acid diimides (NTCDI)<sup>11</sup> and perylene tetracarboxylic acid diimide (PTCDI).<sup>11</sup> A method for the conversion of normally *p*-type molecules to *n*-type is multiple fluorination, thus, perfluoropentacene is an *n*-type material.<sup>12</sup> A more recent advent to small molecules is the introduction of specifically synthesized conjugated oligomers, to be described below. Small molecule organic semiconductors have had their major impact in OLEDs and OFETs. In the former application, metal complexes of organic ligands, particularly aluminum and iridium are the most important. A small molecule that has had a very important place in organic photovoltaics (OPVs) is fullerene C<sub>60</sub>, particularly in the form of two derivatives to be described elsewhere in this document.

The main advantages of small molecules are ease of synthesis and, especially, purification and characterization. Another advantage is ease of processing. Small molecules can be processed into devices from solution or the vapor phase. The main disadvantage of small molecules in devices is that most small molecules tend to crystallize, a serious disadvantage for light emitting devices, where crystallites tend to scatter light as well as cause pin hole formation and loss of contact with addressing electrodes. Another potential problem is migration through the various device layers.

## 2.2 Conjugated polymers.

Macromolecules have been examined for their electronic properties throughout the XX century. In the first half of the century, several researchers examined solids resulting from the pyrolysis of organic polymers. These were generally poorly characterized materials in terms of their chemical structure and composition. The first conducting polymer to be fully characterized was actually the inorganic poly(thiazyl) (SN<sub>x</sub>) which, to this day, is the only superconducting polymer, albeit with a very low transition temperature (*T*<sub>c</sub> 0.2 – 0.5 K).<sup>13</sup> Another polymer was poly(aniline) (PANI). These were mere curiosities until 1977, when Shirakawa, McDiarmid and Heeger, with their coworkers, reported the remarkable increases in conductivity of polyacetylene (PA) upon doping. Their report could be considered the beginning of organic conducting polymers.<sup>14</sup> Though PA turned out to be, essentially, the "fruit fly" of conducting polymers, it did not lead to any applications because it is an unstable solid, reacting exothermically with air and moisture. Nonetheless *p*-doping eventually led to a solid with a conductivity on the order of 10<sup>4</sup> S/cm, a remarkable achievement for a solid consisting only of carbon and hydrogen. In quick succession the polymers based on thiophene [poly(thiophene), PT, poly(3-alkylthiophene, PAT) and phenylene vinylene (PPV) were shown to be stable and dopable to conductivities on the order of 10<sup>3</sup> S/cm. Because the paradigm of the day was still a remnant of research on organic metals, the goal was to achieve higher and higher conductivities until in 1990 Richard Friend and his group reported

the electroluminescence of PPV<sup>15</sup> and in 1992 Sariciftci, et al<sup>16</sup> reported the first bulk heterojunction (BHJ) OPV, thus the emphasis switched to the semiconductor properties of UNDOPED conjugated polymers. Further, all the physics and electronic engineering aspects of organic electronic devices were emphasized from that point on with the chemistry of the materials being guided by device physics and engineering. As is the case with the small molecules, the number of *p*-type polymeric semiconductors is much larger than of the *n*-type conjugated polymers.

The advantages of polymers vs. small molecules are that polymers are natural film-formers with very low tendencies to migrate or crystallize. The major disadvantage is that polymers are very difficult to produce reproducibly with the same molecular weight and polydispersity. They are also more difficult to purify and characterize. Small Oligomers, in principle, have the advantages of small molecules AND polymers

### 3. Basic concepts.

#### 3.1 The solid state.

Organic semiconductors are molecular solids, as contrasted to inorganic semiconductors, which are extended solids. The most attractive feature of molecular solids is that the properties of the solid are essentially those of its constituent molecules. Hence, if one were to increase (or decrease) the  $\pi$ - $\pi^*$  gap of the molecule, the semiconductor energy gap of the solid would follow the same trend. This feature makes the design of organic semiconductors considerably easier than would otherwise be possible. Fortunately this idea can be extended to the design of polymers, where changes in the electronic character of the monomer are reflected directly in the properties of the polymer and the molecular solid derived from the ensemble of polymer chains. Thus, when it was desired to decrease the  $E_g$  of poly(thiophene) ( $E_g$  ca 2.1 eV), decreasing the  $\pi$ - $\pi^*$  gap of the monomer resulted in the decrease of the resulting polymeric solid's  $E_g$  to 1.1eV.<sup>17</sup> Unfortunately the energies involved in forming molecular solids are very small and, as a consequence, molecular solids have a propensity to produce many polymorphs for a given molecule. For example a flat polycyclic aromatic molecule can form at least three different polymorphs: stacks, herringbone or discrete dimmers. The situation becomes even more complicated in the case of polymers. Most polymers form amorphous solids but due to the backbone rigidity of conjugated polymers, they can have crystalline regions interspersed in an amorphous matrix. The crystalline segments can be manipulated by annealing (or tempering) either by heat-treatment or a very small amount of an additive. Polymers can also be coaxed into a relatively ordered state by external fields either mechanical (doctor blade, stretch-alignment, rubbed surface) or electric/magnetic fields for liquid crystalline systems. Ideally all active substrates in organic electronics devices would be crystalline with the molecular ensembles in preferred orientations relative to external influences such as electric field, magnetic field and light but in reality, a new molecule could be designed with, say, improvement in power conversion efficiency (PCE) of an OPV but if its constituent molecules, be they small or macromolecules, refuse to form the proper morphology (polymorph) and cannot be coaxed to order in a desired form, the whole effort can, and will, be derailed. Over the last few decades, rules of self-assembly of molecules into pre-determined structures have been evolving but, so far, incorporation of these to achieve particular goals in organic electronics and

optoelectronics had a very minimal success.

### 3.2 Excitons, electrons and holes.

Charges can be generated in organic semiconductors from the loosely held electrons of  $\pi$  molecular orbitals by heat, irradiation or an electric field. As shown in Fig 1, an OLED is the microscopic reverse of an OPV, the principal species is an

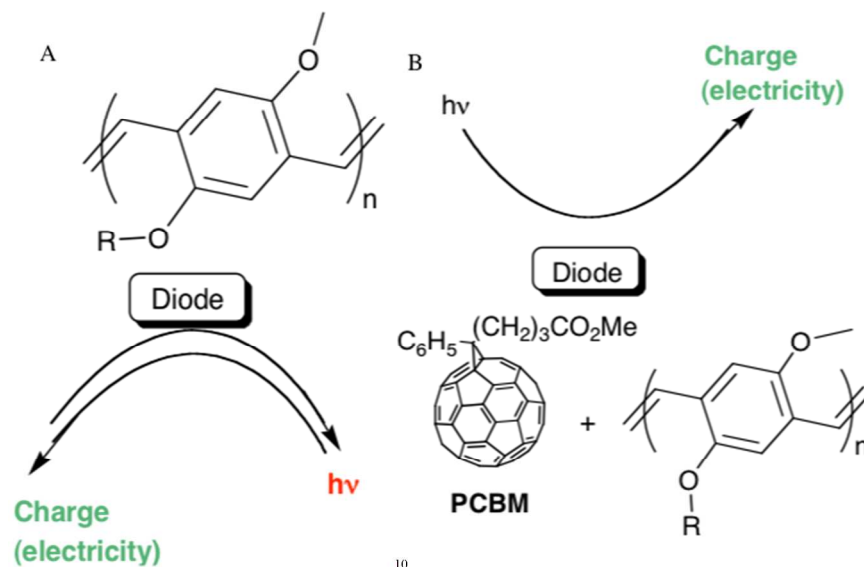


Figure 1. A, schematic representation of the light emission and photovoltaic generation being the reverse of each other; B, improvement of the photovoltaic process by incorporation of the electron acceptor PCBM.

electron-hole pair or exciton. In the light emitter, the electrons and holes are generated at the electrodes, migrate to form excitons and combine, usually at an exciton trapping site, giving off a photon with energy less than the  $\pi$ - $\pi^*$  gap. Conversely, in an OPV, to separate the hole and the electron of an exciton, an acceptor is added to facilitate the charge separation and discourage electron-hole recombination. The excitons are generated by the absorption of photons, the excitons migrate to the D-A interface, where charges are separated, the electron delocalizes along the A component and the positive charge migrates along the D component to their corresponding electrodes

In *p*-type OFETs, the field effect results in ionization of  $\pi$ -electrons (HOMO orbital) with concomitant hole-generation for charge transport. In *n*-type OFETs, the field effect produces a thin electron layer at the accessible sites in the  $\pi^*$  (LUMO orbital) for charge transport.

## 4. Specific devices.

### 4.1 Molecular electronics.

After the first organic metal, TTF-TCNQ, was discovered in 1973, Aviram and

Ratner<sup>18</sup> proposed the first molecular rectifier, giving birth to the field. Over the years, with the advent of scanning probe microscopes, particularly break-junction STM (SMBJ) experiments, the examination of “single molecule” electronic properties was possible. Solomon discussed the thermoelectric properties as a function of  $\pi$ - $\pi$  stacking in a molecular electronics experiment. Not surprising, the theory associated with single molecules is complicated and Baldea showed that current thinking in terms of quantum chemistry may not be absolutely correct. Another aspect of theoretical concern is charge transfer and Venkatramani discussed this aspect of molecular electronics. In the meantime, Venkataraman, discussed implementation of quantum interference to interpret semiconductor properties in molecular electronics such as molecular dependence of resistance ratios. Ottosson discussed the importance of excited state electronic structure on SMBJ. He proposed, based on computational results, that photochemical rearrangements that could occur in a SMBJ could be desirable. Xu discussed his results of contact effects between the electrode and molecule on the properties of the “devices”, in this respect, Xu concluded “Although an individual molecule could perform as a conductor, the produced current is far less than what is required for commercial use. Challenges exist in improving and amplifying the current. Doping special chemicals, metal ions and nanoparticles into individual molecules have been suggested to effectively increase the conductivity of a SMBJ. Attempts towards this direction have just started.”

#### 4.2 Light emitting devices.

Though the first light emitting devices were reported in the early 1960's,<sup>19</sup> they were rather inefficient, it was not until 1987, when Tang and VanSlike<sup>20</sup> reported the first organic thin film light emitting device based on an aluminum organometallic green light emitter, where the efficiency was improved considerably by energy level matching to the cathode and incorporating an organic hole transporting layer (HTL) at the anode to lower the hole transport barrier. With the exception of the addition of an electron-transporting layer (ETL), this architecture remains essentially the same in current devices. Three years later, the first polymer based OLED, a PLED, was reported by the Cambridge group led by Richard Friend. The architecture was considerably simpler, consisting of a thin (ca 100 nm) film of the organic conjugated polymer sandwiched between anode and cathode. Electrons were supplied through an Al contact and holes were collected at an ITO surface. Whereas it was relatively easy to obtain various hues of red and green as well as orange, deep blue was a challenge. Because blue was not so accessible, white organic LED light was also not achievable in the early days but in the recent past several research groups and corporations have achieved white light emission with the well established stratagem of using the high energy blue emission as both color and pump for the other lower energy colors. Figure 2 below is a depiction of a typical “modern” OLED architecture.



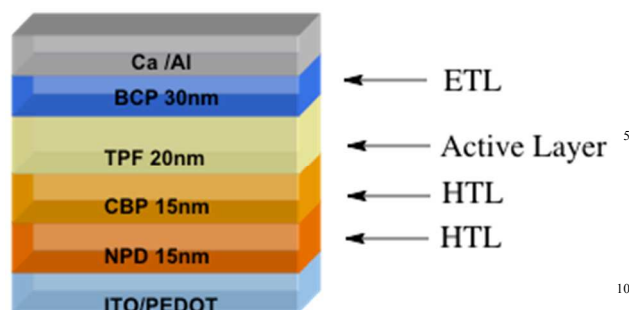


Figure 2. Schematic of a typical OLED, where, where more than one HTL was required to lower the barrier to hole transport. In this case TPF is a blue light emitter and the device was fabricated by vacuum layer deposition

Finally, Forrest and Thompson made a most important contribution by looking at the relative contribution of triplet and singlet excited states to luminescence. They posited, and proved, that devices that exhibited phosphorescence should have dramatically higher efficiencies.<sup>21</sup> It was well known that organic complexes of heavy transition metals such as Pt, Pd or Ir, were efficient phosphorescers. Incorporation of these luminescent molecules into OLEDs was a key step that was required to make these devices commercially important, leading to today's brilliant color Samsung smart phone and television displays. There have been a large number of important contributions, particularly in the recent past to the successful development of organic light-emitting devices and we have seen several of these during the Faraday Discussion. Lemmer discussed an intriguing fabrication improvement through a laser-assisted replication on an inexpensive poly(methyl methacrylate) substrate. Zysman-Colman discussed a novel approach to improve the quantum yield of blue emitters by proper design of the ligand for the transition metal complex. Leo, through his assistant, discussed the effect of scattering, refractive or diffractive elements on improvements of light-emitting devices. Sasaki discussed the possibility of dynamic hologram formation in ferroelectric liquid crystal displays, though these are not OLEDs, their display properties are based on a combination of photovoltaic and alactro-optic effects. Dennany discussed the application of a variant of OLEDs, the electrochemical luminescent (ECL) devices. With a new active star-shaped active organic layer they made very sensitive sensors. Laurand discussed an optically-pumped OLED as a very sensitive microsensor for biological systems that should be useful as label-free biosensing platforms.

#### 4.3 Field effect transistors.

In 1983, the first OFET based on polyacetylene<sup>22</sup> and in 1988 the same device based on polythiophene was reported. These devices, though behaving like classical transistors, showed very low hole mobilities. The first reasonable device was reported by Garnier in 1989<sup>23</sup> and it was based on a small oligomer of polythiophene, sexythiophene and in 1990 the same group reported an all organic device with the SiO<sub>2</sub> insulator replaced by an organic insulator and the glass substrate replaced by an organic plastic film. For vapor deposited thin organic films, the record is 35 cm<sup>2</sup>/Vsec, held by Jurchescu<sup>24</sup> for pentacene and for thin single



crystals, rubrene the record is  $5 - 40 \text{ cm}^2/\text{Vsec}$ .<sup>25</sup> For highly oriented thin polymeric films, oriented on a modified surface, the record is  $36.3 \text{ cm}^2/\text{Vsec}$ .<sup>26</sup> Below (Fig 3) is a depiction of the most popular device fabrications. Most organic semiconductors lend themselves to bottom gate architectures, though in some cases



Figure 3 A “Bottom gate” and B “Top gate” OFET architectures. D, drain; G, gate; S, source; SC, semiconductor.

the best results are obtained with top gate construction. The vast majority of organic semiconductors are p-type but n-type and ambipolar semiconductors have become more numerous in the very recent past.<sup>27</sup> The more interesting of these are the latter, where rather high inverter device gains of  $35^{28}$  and  $86^{29}$  have been reported. Functional OFETs are another more recent entry, also represented by ambipolar devices, particularly in the form of light-emitting devices (LEOFET)<sup>30</sup>, recently reviewed.<sup>28</sup> Though there have been a large number of important contributions, particularly in the recent past to the successful development of organic transistors and we will see several of these as part of these Faraday Discussions, there remain a number of challenges. Most have to do with chemistry. Though the community has been touting the advantages of OFET such as processing simplicity, light weight and flexibility, over the traditional electronics devices; a critical evaluation of the ACTUAL costs involved in mass production, including switching from current synthetic methods to more environmentally friendly ones and to more efficient syntheses of the more complicated molecules, oligomers and polymers has yet to appear.<sup>31</sup> Torsi discussed a hybrid type of thin film transistor (TFT), the electrolyte-gated TFT (EG-TFT). In these devices, the electrolyte serves as a high dielectric layer between the active layer and the gate. By using ZnO as transparent electrode, Torsi’s group has made excellent biocompatible devices. Fabroni discussed organic semiconductor single crystal (OSSC) devices and their application in radiation detection, particularly X-rays. McDouall discussed a theoretical approach to examine the hole mobility in OFETs as a function of structure, particularly the surface structure effects. His results should help the engineering of FETs. Perepichka discussed a very successful crystal engineering result in the design of the active layer of OTFTs. They based their solid state engineering on complementary hydrogen bonding between donor and acceptor components of the crystal, resulting in ambipolar devices. Melzer discussed a system already mentioned by Torsi (above). In these devices, commercial poly(3-hexylthiophene) is used as the active layer and they find that the hole mobility is largely enhanced,

#### 4.4 Organic photovoltaics (OPV, Plastic Solar Cells).

As discussed in relation to Fig 1, above the organic photovoltaic effect is essentially the reverse of the organic light-emitting electroluminescence effect. The main difference is that, in the photovoltaic device, the electron and hole of the exciton

produced by photoexcitation need to be separated before they have a chance to recombine and emit. To achieve this, an electron acceptor is blended into the donor. In the early days of the field, the charge recombination was an apparent insurmountable problem, until the fullerenes were discovered. Nature's fullerene gift has two extremely beneficial properties: i) fullerenes form good *n*-type semiconductor devices with relatively good electron mobilities and ii) the radical anion resulting from electron acceptance is very stable, providing a substantial barrier to electron hole recombination. The early attempts to form bilayer devices with a donor polymer-fullerene interface gave relatively low power conversion efficiencies (PCEs).<sup>16</sup> However, blends with a more soluble derivative of C<sub>60</sub>, PCBM, soon improved the PCE to 2.9%.<sup>32</sup> These blends formed a phase segregated system that naturally formed a bulk heterojunction (BHJ). These BHJ devices are the mainstay of OPV. In the meantime the PCE has been increased to 11.1%.<sup>23</sup> The main theoretical model construct for BHJ was given by Scharber, where they correlated LUMO of the donor polymer with the band gap of the donor and extracted a theoretical PCE. The maximum predicted PCE of a BHJ cell based on PCBM as acceptor was 11%.<sup>34</sup> Nelson discussed a parameter free calculation result of subgap density of states in poly(3-hexylthiophene). One of the main conclusions is that intrachain torsional disorder is much more significant than the interchain coupling disorder in the non-crystalline regions of the solid. Kim discussed organic-inorganic hybrid based solar cells, particularly the stability (or lack thereof) of the hybrid structures toward annealing temperatures. Ponomarenko discussed the design, synthesis and applications of three arm star-shaped molecules in OPV devices. These triphenylamine-based systems can produce up to an impressive PCE of 5.4%.

#### Other devices for the future

The future of organic electronics and photonics is bright, indeed. The new areas into which the science and engineering of organic condensed matter devices are expanding are spintronics and thermoelectrics. In the former, Vardeni<sup>35</sup> recently showed the fabrication of an effective spin valve using Alq<sub>3</sub> as the organic spacer between two ferromagnetic layers and Ando with Sirringhouse recently showed a very exciting spin-charge converter by the use of highly conducting PEDT-PSS.<sup>36</sup> The area of organic thermoelectrics is heating up, with the number of publications increasing from 1 in the 1980's to 70 in 2013.<sup>37</sup>

#### Conclusion and outlook

Research in organic electronics and photonics is a very active field, indeed. The number of publications related to organic electronics involving physics, chemistry, materials science, engineering and biology in the last two decades is astounding and very difficult to measure due to the basic interdisciplinary nature of the endeavour. Fundamental research still dominates the field but several inroads have been made into technical applications and some will be presented as part of this Faraday Discussion. The salient features of the processes in the various devices, viz, molecular electronics, OFETs, LEFETs, OLEDs and OPVs are now relatively well understood. However, many details are still to be worked out, particularly in regards to the end product, namely consumer electronics. For example, in the case of OPV, Cao and Xue conclude:<sup>38</sup>

“Last, but not least, the stability of OPV devices is a critical hurdle that should be tackled before their commercialization. Although OPV devices with a lifetime over seven years have been demonstrated,<sup>39</sup> a more robust encapsulation technology, as well as more detailed study about the degradation mechanism, is required to improve the device stability. In particular, the phase separated bulk heterojunction structure generally is not at equilibrium; thus its morphological stability during operation may be a concern that needs to be better suited”

Some of these concerns can be directly translated from OPV to the other devices described above and in these Faraday Discussions. For example for OFETs, Bao states:<sup>24</sup>

“On the other hand, there are a few challenges the research community has to overcome before OFETs can take off for practical applications. Organic circuits are generally featured as low cost electronics, even though there is still lack of a comprehensive and accessible analysis of cost-structures of OFET devices for various applications. From the aspect of synthetic chemistry, there are a few cost drivers, namely, reaction steps and yields, reagents and solvents, as well as purification approaches.....Unfortunately, the majority high performance OFET materials are currently processed from chlorinated solvents. It is thus important for chemists to develop OFET materials that can be processed from nonchlorinated solvents, while retaining high performance. Bao further concludes:<sup>24</sup>

“Some other issues for OFETs include (1) the long-term storage and operation stability of the devices, (2) the reliability and reproducibility of the devices, and (3) the patterning and integration of OFETs in integrated circuits. To create solutions for these challenges, not only are OSC [organic semiconductors] design and processing important, but the advancement of dielectric and encapsulation materials is also crucial. In addition, environmental assessment of OSCs is needed, since they are aromatic compounds and likely to be carcinogens. This is especially critical, if OFETs are ever used in disposable devices”

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