



## Review

## Challenges in organometallic research – Great opportunity for solar cells and OLEDs

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## ABSTRACT

Organometallic molecules have become a field of intense activities in the optoelectronic research. They hold great promise as versatile functional materials for use in energy interconversions. This special issue presents a critical perspective of the field, with emphasis on fundamental concepts and current applications. Practical applications are enumerated and illustrated by an example. These include systems where light is transformed into electricity and vice versa. New synthetic methods need to be developed to produce technologically useful materials with specific functional roles.

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## 1. Introduction

Since the quality of our life depends to a large extent on the availability of energy, the energy crisis problem will pose a great threat to us for the foreseeable future and energy is and will certainly remain one of the great challenges for the world. It is critically essential to find alternative forms of renewable energy sources [1]. Currently, people are talking about “alternative energy” or “renewable energy” in various scientific disciplines around the world and these terms are frequently brought to wide public attention. There is great interest in developing renewable resources and improving the technologies for energy interconversions. The transformations of light into electricity (electrical energy generation in photovoltaic cells) and electricity into light (light generation in light-emitting diodes) are two important interrelated areas that have attracted considerable research interest in recent years (Fig. 1). Organometallic compounds have been sought and

investigated for both these transformations and these metal complexes and polymers will undoubtedly play key roles in its safe and efficient production, transformation and utilization [2]. The chemical and physical properties of such organometallic materials can be easily fine-tuned simply by varying its chemical structures to develop the best materials to fit a particular energy conversion application.

## 2. Energy generation from photovoltaic solar cells

In an attempt to reduce the use of fossil fuels which are not eternal and heavily contribute to global warming, scientists are looking for other sustainable energy sources to serve our future energy needs. Of these, solar energy is promising because the Earth receives more energy from the Sun in one hour than is used by all humanity in the course of an entire year. Much research has gone into producing efficient solar cells, the devices which convert sunlight to electricity through a process called the photovoltaic effect. Photovoltaic devices are able to convert sunlight directly into electrical energy. Solar energy is regarded as renewable energy. It is

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Fig. 1. The interplay in energy conversion between solar cells and organic light-emitting diodes.

environmentally friendly, abundant and also free. Therefore, direct photoconversion of solar energy by using photovoltaic technology is increasingly recognized worldwide as a viable hi-tech solution to the growing energy challenge [3,4].

Currently, solar cells are made largely from inorganic semiconductors (e.g. highly purified silicon crystals), similar to those used in computer chips, but these inorganic semiconductors are expensive because they require high purity crystals and need to be fabricated in vacuum. So, researchers are seeking new inexpensive alternatives. Research into organic and organometallic molecules (in the form of both small-molecules and macromolecules), has recently shown great promise. Organic solar cells attract considerable attention due to their unique advantages, such as low cost, lightweight, ease of solution processability and potential use in flexible and large-area devices [3–6]. Unfortunately, broad applications of organic polymer solar cells are currently limited by the low power conversion efficiency (PCE) and photocurrent as compared to those of the inorganic semiconductors [7–9]. The low PCE has limited progress towards commercialization. Encouraging progress has been made over the past few years in the field of photovoltaic solar cells using organic polymers [7–10]. The prototype organic polymer in this area is poly(3-hexylthiophene) (P3HT) in which a PCE as high as 6.5% is achieved with a tandem cell architecture [11]. A useful alternative was recently developed by Wong et al.

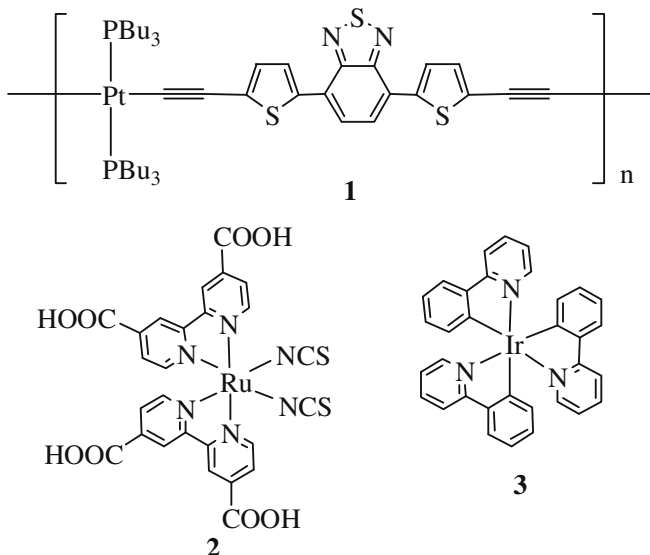


Fig. 2. Chemical structures of 1–3.

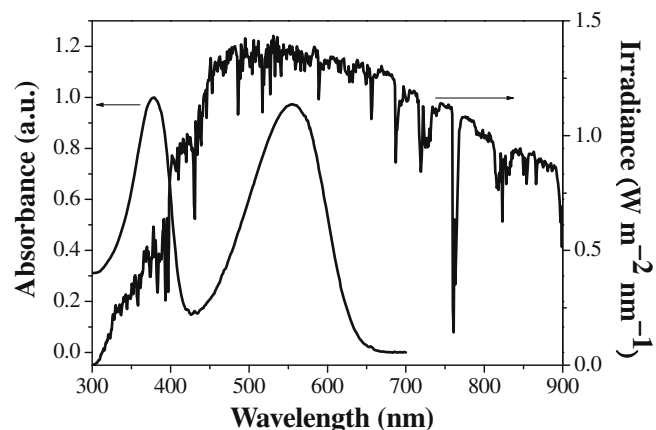


Fig. 3. Absorption spectra of **1** in  $\text{CH}_2\text{Cl}_2$  at 293 K, showing a good spectral match with the standard AM 1.5 solar spectrum (AM = air mass).

using a low-bandgap organometallic polyyne polymer **1** which shows a PCE of  $\sim 4.1\%$  (Fig. 2) [12]. It is anticipated that these strongly absorbing conjugated organometallic congeners will make important contributions to identify environmental friendly hi-tech solutions for the energy problem (Fig. 3) [13].

In general, there are two types of organic solar cells commonly in use, namely, bulk-heterojunction solar cells (BHJSCs) [14] and dye-sensitized solar cells (DSSCs) [5,15]. The BHJSCs are typically made by sandwiching a thin film of photoactive polymers between two electrodes such as indium tin oxide (ITO) and aluminum (Fig. 4a). Poly(3,4-ethylene-dioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layer improves the surface quality of the ITO electrode as well as facilitates the hole injection/extraction. The interpenetrated electron donating and accepting components at the nanometer length scale are made simply by dissolving organic/organometallic absorber and electron-accepting methanofullerene in the same solvent and then casting a blend (Fig. 4a). The active material (i.e. electron donor such as P3HT) behaves as the photosensitive absorber of the sunlight and releases electrons to the electron acceptor such as [6,6]-phenyl- $\text{C}_{61}$ -butyric acid methyl ester (PCBM). There are four essential steps for the conversion of light into electricity in organic solar cells: (1) absorption of a photon leading to the formation of an excited state (i.e. the creation of bound electron-hole pair (exciton)); (2) exciton diffusion to a region where exciton dissociation (i.e. charge separation) occurs; (3) charge transport of electrons and holes within the organic semiconductor to the respective electrodes, and finally (4) the photocurrent generation which can then be used to do work or charge a battery. Each of these steps must be optimized by a suitable

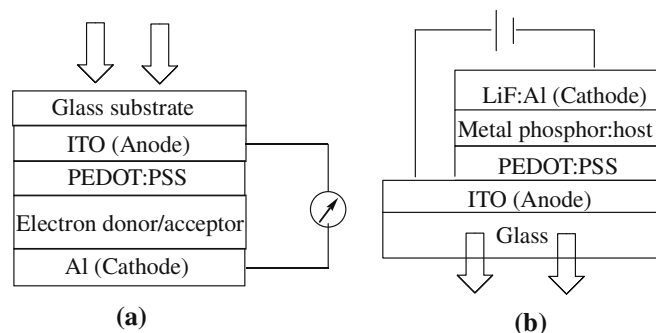


Fig. 4. (a) Schematic diagrams of a BHJSC structure and (b) a typical OLED structure derived from an organometallic phosphor.

molecular design in order to achieve the best overall cell performance.

A typical DSSC consists of two glass plates coated with a transparent conductive oxide layer. The working electrode is covered with a film of a dye-sensitized substance and the counter electrode is coated with a catalyst. Both plates are sandwiched together with the gap between them filled by an electrolyte. Light absorption is carried out by dye molecules in which the absorbed photons cause dye photoexcitation to release an electron rapidly to the semiconductor. The injected electrons then hop through the colloidal TiO<sub>2</sub> particles to reach the collector. Following this, the electron passes through an outer circuit to reach the other transparent conductive oxide layer at the counter electrode, ultimately doing electrical work for the user. Finally, the electron is transferred to the electrolyte where it reduces the oxidant and the reduced form reduces the excited dye to the ground state and completes the circuit. Organometallic donor materials are widely used in DSSCs in which the Grätzel-type cell based on **2** owes much success to this work [5,6,16]. Over the years, a large number of other related dyes have been reported in the literature [2,15]. In these types of cells, ruthenium(II) dyes have played a prominent role and PCEs as high as 11% using AM1.5 conditions have been obtained [17,18]. Organometallic complexes of other transition metals including Re<sup>I</sup>, Os<sup>II</sup> and Ir<sup>III</sup> have attracted increasing attention in recent years [19–21].

### 3. Efficient electrophosphorescence from organic light-emitting devices

While solar cells use sunlight to produce electricity, another stream of current research focuses on the reverse of this process, that is, using electricity to produce light as exemplified in organic light-emitting diode chemistry. Recent research on organic light-emitting diodes (OLEDs), has been focused on devices composed of thin films containing organic/organometallic molecules that directly convert electricity into light (Fig. 4b) [22]. OLEDs may revolutionize display technologies in the scientific community. The key advantages of OLEDs for flat-panel display applications are their self-emitting property, high luminous efficiency, full color capability, wide viewing angle, high contrast, low power consumption, low weight, potentially large-area color displays and flexibility [23–26]. Unlike liquid crystal displays (LCDs), OLEDs lend themselves to the display applications because they can be printed onto a surface using an inkjet or even screen printing technology. They are also more energy-efficient and are generally lower in cost than LCDs. In view of this, the rapidly growing market for OLED technology is driving both the academic and industrial communities toward the development of new functional materials for advanced manufacturing technology. Heavy metal organometallic complexes have recently gained tremendous research interest for fabricating highly efficient phosphorescent OLEDs by taking advantage of the 1:3 exciton singlet/triplet ratio predicted by simple spin statistics [27–29]. These phosphorescent emitters are mainly derived from the family of the third-row transition metal (Re<sup>I</sup>, Os<sup>II</sup>, Ir<sup>III</sup> and Pt<sup>II</sup>) complexes [30–33], although examples with some second-row transition metals such as Ru<sup>II</sup> are also known [32]. The three key electronic processes, namely, (i) charge injection, (ii) charge transport, and (iii) electron-hole recombination (i.e. exciton formation) efficiency must be separately optimized in order to improve the overall OLED performance. The pioneering work by Forrest and Thompson based on the utilization of triplet emitters rather than of singlet emitters was a breakthrough in tackling the recombination efficiency issue [34], and has since triggered a substantial amount of research activities on phosphorescent molecules with much success. This strategy enhances light emission efficiency by the efficient electrophosphorescence. The advantage of triplet

emitters over the singlet-emitting counterparts is that they can capture energy from both singlet and triplet excited states, lifting the upper limit of the internal quantum efficiency of the usual fluorescent dopant-based devices from 25% to nearly 100%. Phosphorescent emitters with heavy metal ions allow for circumvention of this limitation if the excitons generated by hole-electron recombination reside at a site where efficient spin-orbit coupling leads to efficient singlet-triplet state mixing which eliminates the spin-forbidden nature of the radiative relaxation of the triplet state. Of all the systems investigated to date, [Ir(ppy)<sub>3</sub>] (**3**) [35] and [Ir(ppy)<sub>2</sub>(acac)] [36] (Hppy = 2-phenylpyridine, Hacac = acetylacetonate) are the most well-studied compounds in this area. Neutral iridium(III) cyclometalated complexes have been widely employed as phosphorescent dyes in high-efficiency OLEDs with external quantum efficiency of up to 19% using the multilayered device structure [37]. The phosphorescence color tuning capability of these metalophosphors proceeded via relevant modifications of the ligand structures and has been well documented for important applications in full-color displays [38–40]. While the electronic properties of metal-organic materials are characterized by preferential hole transport and low carrier mobilities, additional work is still required to optimize OLED efficiency by maximizing the carrier transport and mobility of both the holes and electrons through tailoring of the chemical structures of the phosphorescent dyes [41].

### 4. Epilogue and outlook

To draw a simple conclusion here, organometallic chemistry can and will make an important contribution to the global energy problem. In this critical issue, a large number of renowned scientists have reported on the different types of organometallic molecules and polymers that can function as molecular materials for energy conversion. These metal-containing compounds are very useful in energy-generating (solar cells) and energy-saving (OLEDs) applications and we can look forward to these continuing developments with substantial optimism. In several cases, there are examples of molecules that can even serve as bifunctional materials and can be applied both in solar cells and in OLEDs. Multifunctional and ionic metalophosphors represent a key emerging field and many exciting future challenges exist for both exploratory and applications-oriented research. The latter area has great potential to excel in the realization of light-emitting electrochemical cells (LECs) [42–44]. The potential of exploiting white OLEDs as next-generation illumination sources and backlights for LCDs is also worthy of intensive investigation [45,46]. To harness their strengths and turn the challenges into opportunities, collaborative efforts from colleagues from a variety of cross-disciplines are needed and we anticipate a brighter future to extend for many years to come.

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