

Organic photonics and organic optoelectronics

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The following reports were put on the session agenda as posted on the website www.gpad.ac.ru of the RAS Physical Sciences Division:

(1) **Vitukhnovsky A G** (Lebedev Physical Institute, RAS, Moscow) “Organic photonics: achievements and setbacks”;

(2) **Aleshin A N** (Ioffe Physical Technical Institute, RAS, St. Petersburg) “Organic optoelectronics based on polymer–inorganic nanoparticle composite materials.”

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Organic photonics: achievements and setbacks

A G Vitukhnovsky

1. Introduction

Organic photonics is a relatively new area of science and industry related to the production of optical devices of organic materials on a common technological platform. The main advantage of organic photonics is the low cost of the production technologies and materials, and the flexibility of devices made of organic materials. Scientific investigations performed in the area of organic photonics are aimed at the development of new-generation telecommunication and computer technologies and photovoltaic (PV) [1] and organic light-emitting diodes (OLEDs) [2].

The past ten years have seen tremendous progress in the area of OLED technology. It has been possible to solve the problems of the internal efficiency in the use of phosphorescent dyes and to achieve progress regarding stability. The stability and efficiency of blue light-emitting diodes can be improved even further, but the parameters already achieved are quite sufficient for many applications. Despite major progress towards achieving a high internal efficiency (close to 100%) of energy conversion, there is still the potential to

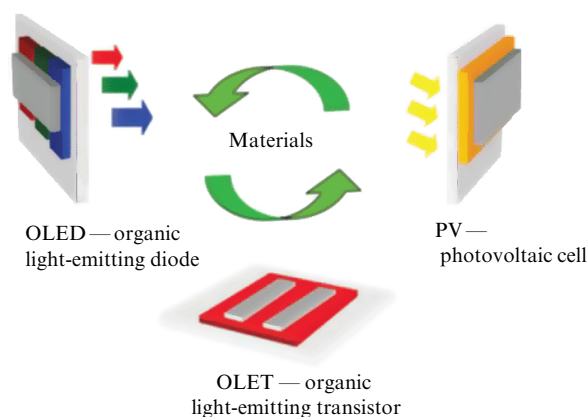


Figure 1. Organic photonic devices.

improve the external energy conversion efficiency for OLEDs.

Many mobile phones are already produced with the use of OLEDs, but the solution to production problems for large displays is currently too expensive. This is the reason why large companies enter the market first. For instance, Sony made an OLED TV set — and it does look spectacular — at a price of several thousand dollars, which is currently more like a demonstration of technical and financial resources than a mass-market product.

Despite the demonstrated progress in OLED technology, several processes (exciton quenching, photon loss, etc.) limit the breadth of its application and call for a search for new approaches to improve the efficiency and brightness. Organic light emitting transistors (OLETs) are alternative light sources, which combine, for a similar design, the thin film transistor (TFT) mechanism and the electroluminescence of organic materials. Therefore, OLET technology is a radically new advance in organic photonics. An impressive achievement in the area of OLET technology is the development of a device with three emissive layers and an external quantum yield of 5%, comparable to the similar parameter for OLED devices [3].

Figure 1 shows schematic diagrams of organic photonic devices, in which some achievements deserve special mention.

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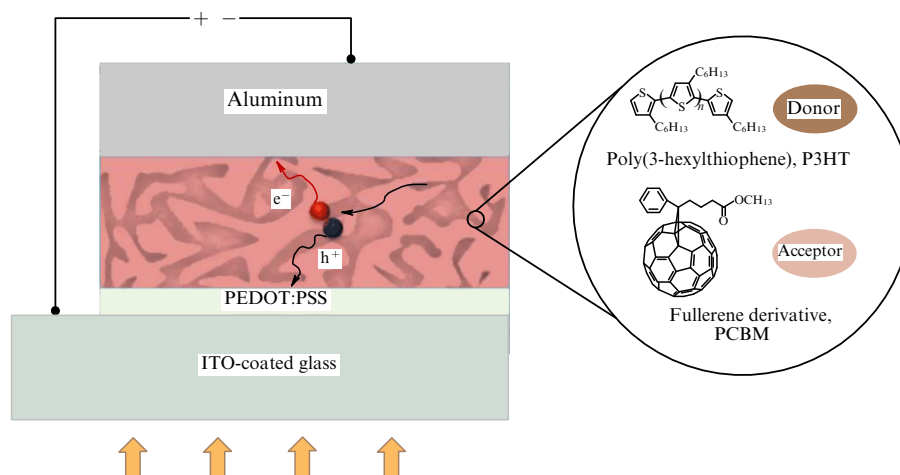


Figure 2. Light conversion in an organic solar battery (a PV cell). PEDOT:PSS — poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate), ITO — indium-tin oxide, PCBM — [6,6]-phenyl-C61-butyric acid methyl ester.

2. A little about organic photovoltaics

Organic photovoltaics (PVs) have been making rapid strides during the last ten years, but nevertheless rank well below OLEDs in maturity. Although the PV technology is free of the problems inherent in the OLED technology, the stability of organic compounds is a serious problem in connection with the inevitable action of solar irradiation. To date, PV technology has not been able to compete with traditional inorganic technologies. Competing technologies, for instance, those using cadmium telluride (CdTe), have presently reached a cost of 1 dollar per watt, while the cost of materials is estimated at less than 0.05 dollars per watt, which leaves almost no room for organics. The efficiency is of paramount importance, and considerable progress has been made in this area, especially with the use of polymers. An efficiency above 6% has been achieved by introducing fullerenes into organic solar elements. This is a significant improvement, which inspires optimism. Reports about overcoming the 10% barrier, which appear in the literature, should be treated with caution, although it is precisely overcoming the 10% barrier which opens the way for the wide commercial use of organic PV cells.

An organic solar cell consists of an active layer located between two electrodes (Fig. 2) [4]. When such a system is illuminated by an external source, the active layer absorbs photons to produce charge-carrier pairs (excitons). For this cell to be efficient, the photogenerated excitons should decay into independent carriers—conduction electrons (e^-) and holes (h^+)—to provide charge accumulation at the electrodes. Furthermore, the decay must occur within the lifetime of the excitons in order to avoid recombination. The standard thickness of the active layer in organic solar batteries is 100–300 nm, which provides almost complete radiation absorption in the spectral band about the wavelength of 530 nm. But the efficiency of this solar cell is limited owing to the short exciton diffusion path in the organic active layer and the low mobility of the free carriers (electrons and holes). As a result, few charges find their way to the electrodes, and hence the total conversion efficiency turns out to be low. These negative factors can be partly compensated by decreasing the active layer thickness to 50 nm; however, this lowers the efficiency of light absorption and does not allow substantially improving the total efficiency.

The use of metallic nanoparticles permits increasing the absorption of light in superthin active layers. Owing to the high intensity of the electromagnetic field in the vicinity of nanoparticles, the probability of exciton dissociation increases. Furthermore, the fraction of absorbed photons increases due to scattering. Because the optical properties of nanoparticles are largely dependent on their size, it is possible to optimally ‘tune’ the solar battery absorption peak.

The efficiency of energy conversion in cells containing gold nanoparticles 50 nm in diameter is simultaneously estimated from three factors: the fraction of absorbed photons, the efficiency of exciton dissociation, and the efficiency of charge collection at the electrodes. Using gold nanoparticles, it is possible to increase the energy conversion efficiency by 65% (for the same thickness of the active layer) [5, 6]. A Nozik proposed another promising concept to improve the efficiency of organic solar batteries with the use of semiconductor nanocrystals [quantum dots (QDs)] introduced into the organic matrix [7]. Exciton multiplication (multiexciton generation, MEG) was experimentally demonstrated to occur in semiconductor colloidal quantum dots—an effect that does not occur in bulk semiconductors [8].

It was shown that a photon with the energy 7.8 times higher than the energy gap E_g (Fig. 3) exhibits a thermal loss of 10%, while for the ‘ordinary scenario’, the loss amounts to

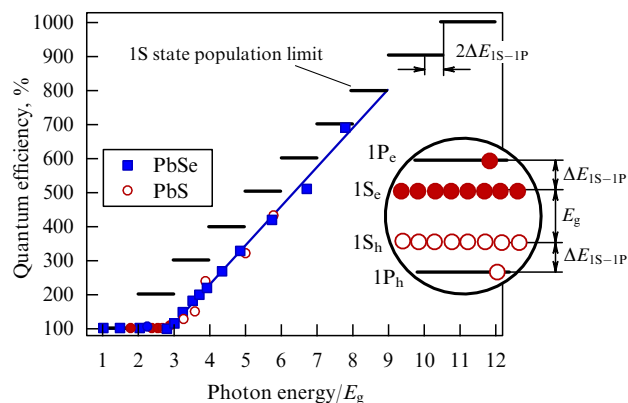


Figure 3. Effect of exciton multiplication [8].

about 90%. As a result, the efficiency of photon–exciton conversion exceeds 700% (sic!). This circumstance is highly attractive for the production of high-efficiency solar batteries. However, there is a limiting factor as well: the charge transfer from a colloidal quantum dot to the electrodes is far from efficient, and a realistic design of the device has not been proposed so far.

3. More about light-emitting organic devices

The well-known phenomenon of light emission in the passage of current through semiconducting materials is widely used in inorganic light-emitting diodes, where the passing current produces electron–hole pairs (excitons) in the semiconductor, which emit light in a specific wavelength range in the course of subsequent recombination.

By the mid-1980s, it had been shown that some synthesized organic substances, specifically those based on so-called small organic molecules [9] and polymers [10], are capable of converting electric current into visible light. Certain advantages of organics are worthy of mention.

First, there is the property inherent in organic semiconductors and absent in inorganic ones, which allows varying the OLED emission spectrum over relatively wide limits by changing the structure of light emitters (organic molecules) and using copolymers or so-called small molecules, as well as their combinations. This opens up possibilities for making materials capable of emitting light of highly diverse colors and shades.

The second important property that gives enormous advantages to the new materials is the manufacturability of light-emitting devices. Layers of small organic molecules can be deposited by the well-known methods of vacuum or centrifugal deposition, which allow using long-developed equipment and thereby making production cheaper. As regards polymer-based OLEDs, it is possible to use jet printers; in this case, semiconductor polymers are dissolved in the corresponding organic solvent and deposited with the help of a jet printer on a glass or plastic substrate.

An OLED pixel is rather simple in structure (Fig. 4). Unlike a liquid-crystal or plasma display, an OLED display does not require two pieces of glass; one piece, which is the anode, is sufficient, on which a transparent conducting material, indium-tin oxide (ITO), is deposited. Deposited next are organic material layers (hole- and electron-conductive transport layers) and an emissive layer approximately 100 nm in thickness, in which electron–hole recombination events and the production of light photons occur. For a cathode, a thin layer of a metal alloy with a low electron work function is used (for instance, aluminum-coated lithium fluoride).

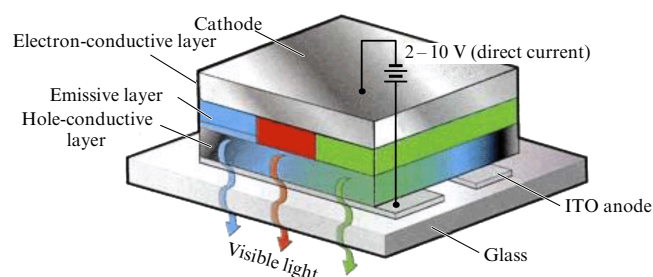


Figure 4. Structure of an organic light-emitting diode.

We emphasize a crucial difference between an OLED pixel and a liquid-crystal one. In the former, the pixel is an active element (it emits light), while in the latter, the pixel is a passive element (light reflected from liquid crystal molecules is used). Furthermore, OLED-technology-based displays are notable for the low energy consumption, high contrast ratio (owing to the active light emission), short pixel response time, low weight, and small thickness; all this gives great advantages to this technology over liquid-crystal and plasma technologies.

For a display substrate, flexible transparent plastic rather than glass can be used. In this case, the organic sandwich is a thin flexible structure; for developers, this opens up broad possibilities for making information display devices of radically new quality and for completely new applications.

Even nowadays, OLED displays enjoy wide use. They are primarily small displays with immediate addressing (passive arrays) for pocket electronic devices like cell phones, MP3 players, and digital cameras. The first commercial OLED device of this category was a monochrome display for a car radio manufactured by Pioneer Ltd. (Japan) since 1997.

At present, leading research and technological centers are pursuing intensive research and development of new composite nanomaterials and photonic and optoelectronic devices that use diverse hybrid nanostructures [11, 12]. In particular, efforts are underway to develop organic light-emitting devices [13, 14]. Of special interest for the development of OLED devices are multilayer nanostructures that comprise organic matrices and semiconductor colloidal core–shell quantum dots of spherical or more complex shapes introduced into the matrices (for instance, CdTe/CdSe nanotetrapods [15]).

Organic light-emitting diodes (QD-OLEDs) made around such structures [16, 17] offer several advantages over ordinary OLEDs. This is due to the unique optical properties of colloidal quantum dots, among which are a high luminescence efficiency and the possibility of tuning the radiation wavelength in a wide spectral range.

A multilayer nanostructure-based light-emitting diode in which the role of the emitter is played by semiconductor colloidal CdSe/CdS quantum dots (QDs) was developed in the Lebedev Physical Institute (LPI), Russian Academy of Sciences [18]. The absorption and photo- and electroluminescence spectra were obtained. Quantum size effects were shown to strongly affect the spectral and electronic characteristics of the diode. The rate of excitonic excitation energy transfer from organic molecules to quantum dots was shown to increase by more than an order of magnitude upon decreasing the diameter of the particle core, CdSe, from 5 to 3 nm and to significantly depend on the thickness of the particle shell, CdS. Figure 5 shows the structure of a model QD-OLED in which Alq3 (tris(8-hydroxyquinolinato) aluminum) was used as the electron transition layer (ETL) and TPD (N,N'-bis(3-methylphenyl)-N,N'-bis(phenyl)-9,9-spiro-bifluorene) was used as the hole transition layer (HTL). Possible mechanisms of quantum dot excitation are shown in Fig. 5b.

The transfer rates for each conductive layer (see Table 1) were estimated using the quantum dot absorption spectra and

Table 1. Donor–acceptor transfer rate K_{D-A} from TPD and Alq3 to quantum dots.

K_{D-A} TPD	K_{D-A} Alq3
$1.1 \times 10^9 \text{ s}^{-1}$	$5.5 \times 10^7 \text{ s}^{-1}$

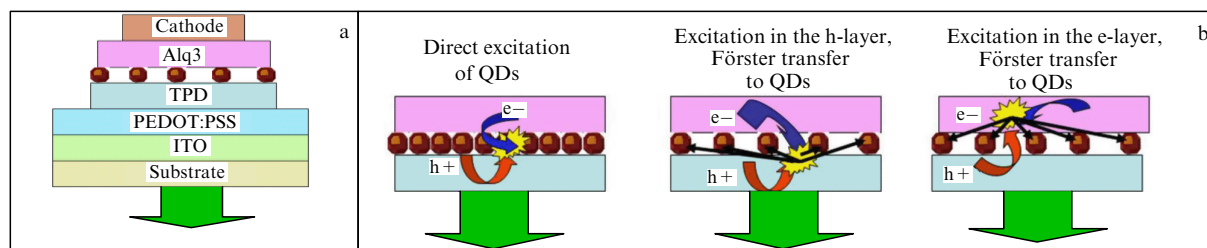


Figure 5. QD-OLED structure and different QD excitation mechanisms. (a) QD-OLED structure. (b) Layer of CdSe/CdS quantum dots between ETL (Alq3) and HTL (TPD).

the luminescence spectra for the materials of the hole- and electron-conductive layers, as well as the classical Förster expression for electronic excitation transfer rates [19]. A conclusion was drawn about the transfer of electronic excitation from TPD to the quantum dots with a CdSe core 3 nm in diameter and a CdS shell 0.5 nm in thickness.

These investigations suggest that varying the core and shell sizes of CdSe/CdS quantum dots as well as their arrangement density in the active diode layer allows not only substantially affecting its spectral characteristics (including the wavelength and linewidth of emission) but also significantly modifying the rate of excitonic excitation transfer from donor organic molecules to the quantum dots.

Along with the variation of the quantum-dot arrangement density in the active diode layer, this permits exerting a strong effect on the electronic characteristics and the efficiency of device operation. The resultant estimates also give the characteristic spacing between the p–n junction domain (in which exciton production occurs in organic molecules at the interface between the transport diode layers) and the domain that should accommodate the layer of quantum dots for the efficient operation of a QD-OLED device. The research demonstrates the possibility of efficiently controlling the spectral characteristics and electronic process rates in nanophotonic devices involving quantum dots introduced into an organic matrix.

4. Conclusions

Despite the obvious achievements of OLED technology, which are constantly demonstrated at recent display industry expositions, a large number of problems remain to be solved; to some extent, these problems impede the fast commercialization of the products. In particular, companies and research centers are pursuing vigorous investigations to obtain more stable and cheaper organic materials and to lengthen their lifetime or the time during which the organics that operate in displays retain the requisite brightness level.

The most acute problem encountered by the OLED display branch of the industry has only an indirect bearing on the OLED materials themselves. However strange it may seem, this is the stability of not only the organic compounds but also the silicon substrate. Unlike the emission of displays manufactured by other technologies, the emission of OLED displays is proportional to the injected current, making them particularly sensitive to the degradation of the transistor board that is responsible for their switching on and off. That is why active-matrix OLED displays require especially reliable and stable control transistors. Therefore, display manufacturers have been forced to use polycrystalline silicon for transistor boards instead of cheaper amorphous silicon. Investigations aimed at solving this problem continue, with

companies endeavoring to develop new materials or new methods of annealing, but the problem still persists. Another problem consists in the patterning of displays, i.e., in pixel definition. Currently, the industry uses mostly shadow masks, which are perfectly suited for small displays but are hardly scalable to large sizes. Big masks bend and produce dust, and both of these are manufacturing problems. It is likely that the development of efficient OLET devices will resolve this painful problem. Although the development of materials and structures continues, the majority of the basic problems have only been partly solved, and the problems in manufacturing efficient OLEDs deserve special attention.

Judging by the number of research centers and companies involved in research and development and by the amount of capital invested, the production of OLED displays is one of the most rapidly growing industries in the world. Samsung SDI, RiTdisplay, Pioneer, Univision Technology Inc., and Philips are the world top five companies delivering up to 80% of OLED panels to the market today, with Samsung's share amounting to about 50%. According to iSuppli, an American research company, about 40 institutes and enterprises are involved in OLED technologies in China. In several countries, scientific research and development have governmental support at the level of national programs; such programs exist in the USA, Japan, the European Union, and China. It is regrettable that a similar national program does not exist in Russia, where research in this extremely promising area of organic photonics is pursued by a small number of scientific groups.

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Organic optoelectronics based on polymer–inorganic nanoparticle composite materials

A N Aleshin

Nanocomposite materials based on conducting polymers and inorganic nanoparticles are of great interest due to their practical applications in organic electronic devices such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), solar batteries, and memory cells [1–5]. Elements of organic electronics based on polymer–inorganic nanoparticle hybrid materials are compatible with printing organic electronics technology, which is currently one of the most promising due to its high efficiency and low net cost.

The integration of organic materials (polymers) and inorganic materials (nanoparticles) at the nanolevel can be used to manufacture optoelectronic structures combining 3D polymer matrix technology with the unique electric and optical properties of inorganic nanoparticles (0D quantum dots ~ 10 nm in size). Both components operate together in such structures, providing control of the radiation color emitted by OLEDs. The emission spectrum depends on the polymer type and the type, size, and functioning of nanoparticles. In particular, to obtain white emission, materials emitting in the blue, green, and red (or blue and orange) spectral regions must be combined in one structure. The combination of emitters operating in different spectral regions requires understanding and controlling charge-carrier transfer processes in such systems, where the exciton transport from a wide-band (blue) emitter to a narrow-band (orange, red) emitter can lead to emission of light only from the narrow-band material for a 100% energy transfer efficiency.

The control of charge transfer processes for achieving the successive emission of light from all materials contained in the active layer of an OLED is the most important problem for obtaining white emission. This problem can be resolved by

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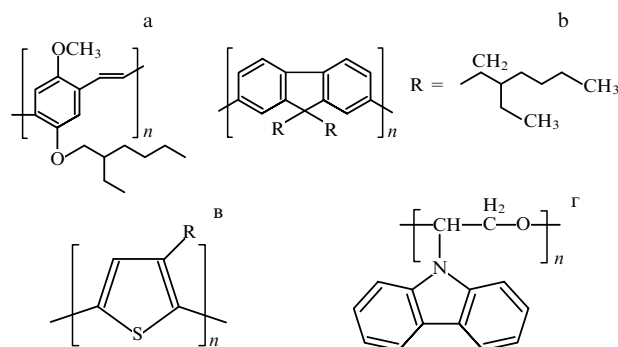


Figure 1. Molecular structure of semiconductor polymers used in organic electronic devices: (a) MEH-PPV (poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene]) ($E_g \approx 2.34$ eV); (b) PFO (poly(2,7-9,9-di(oxy-2,5,8-trioxadecane)fluorene)) ($E_g \approx 2.9$ eV); (c) P3HT (poly(3-hexylthiophene)) ($E_g \approx 2.0$ eV); (d) PVC (poly(N-vinylcarbazole)) ($E_g \approx 3.6$ eV).

combining the optimal selection of emitting components in the active layer, their relative concentrations, and the possibility of controlling their interaction at the molecular level.

One of the promising ways for manufacturing low-cost, large-area white OLEDs deposited from solution onto substrates by jet printing methods is the combination of several emitting materials in one active layer. This approach uses the mixing of two or three polymers in the active layer, which emit in different spectral regions, thereby controlling the emission color, or doping a wide-band material with a narrow-band material, the wide-band material being a medium for the charge carrier transfer. Important in this field are the development of white OLEDs based on a polymer mixture [6, 7] and the creation of polymer–inorganic nanoparticle hybrid active layers for white OLEDs [2]. Recently, we investigated the properties of the polymer–inorganic nanoparticle hybrid active layers that we obtained for white OLEDs [8–12] and OLEDs based on polymers doped with polymer nanoparticles [13] emitting in different spectral ranges, from UV to IR.

The polymers that we studied (derivatives of polyphenylene vinylene (PPV), polyfluorene (PFO), polyvinylcarbazole (PVC), etc.), with the structural formulas shown in Fig. 1, are soluble in usual organic solvents, while inorganic semiconductor particles (ZnO, Si, CdS, CdSe, etc.) deposited from solutions had diameters of 10–50 nm and the band gap E_g from ≈ 1.8 eV (Si) to ≈ 3.35 eV (ZnO). This opens up possibilities for the deposition of composites from solutions on both ordinary glass substrates and flexible substrates using jet printer technology. The parameters of OLEDs based on multilayer composite structures are expected to be higher than these of purely polymer OLEDs due to the efficient radiative recombination in both the polymer and nanoparticles, and also in their complexes [2]. An important advantage of composite OLED structures is that the characteristic relaxation times of charge carriers in them are considerably shorter (by two–three orders of magnitude) than those in structures based on liquid crystals, while the doping of a polymer matrix with inorganic nanoparticles slows down the degradation of a hybrid structure, thereby increasing the life of such devices.

As shown in [8–12], the use of composite active layers in OLEDs based on semiconductor conjugated polymers and