

# Colours from electroactive polymers: Electrochromic, electroluminescent and laser devices based on organic materials

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## Abstract

This paper focuses on the most relevant devices currently used in order to achieve electrically stimulated generations of colours from electroactive polymers, either as coloured light emissions from the material or as modifications of its intrinsic colour properties. For this purpose, most relevant materials, fundamental principles of operations, latest developments and current applications of organic-based electrochromic, electroluminescent and lasing devices are reviewed here. The very promising performances resulting from the analysis of state-of-the-art products, and in particular of those which are currently approaching commercial applications, suggest likely roles played by such devices for niche applications in the very near future.

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## 1. Introduction

A material can be defined *electroactive* if it responds to an electrical stimulation with a reversible variation of one or more physico-chemical properties. The electroactivity of a material can be evaluated in several respects. In relation to the particular effect investigated, definite output variables are taken into account in order to quantify the material response. Owing to the ease of generation and processing of input signals of the electrical type, electrically responsive materials with tailorable functionalities (as electroactive polymers are) are considered today as smart materials.

For many years, several types of electroactive polymers (EAPs) and organic macromolecular compounds have been widely investigated for different kinds of applications, including chemical and physical sensors, actuators and a large number of electronic and optoelectronic devices [1]. Among the last two classes,

most notable examples are represented by electron and ion conductors, photoconductors, batteries, photovoltaic cells, supercapacitors, field-effect transistors, optical memories, light-emitting diodes, photodiodes, electrochromic and photoelectrochromic components and even lasers [2–8]. The continuous demand for new products requiring novel solutions, unthinkable until a few years ago, is today greatly driving such investigations, in order to replace conventional electric, electronic and optoelectronic devices with smart plastics capable of offering improved functioning in many niche applications. Electronic/optoelectronic components for portable, flexible or even wearable systems like keyboards, displays, sensors and processors used for personal information and monitoring are just some examples of possible fields of application of organic electroactive materials [1].

Such a trend is encouraged not only by already demonstrated and continuously improving tunable active performances of organic materials, but also by the high mechanical flexibility (compliance) offered by most of the organics, overcoming the typical stiffness of inorganic materials (such as silicon). Moreover, organics offer low weight and low cost, combined with a

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remarkable ease of processing techniques like spin coating, ink-jet printing or casting typically used for organics become inexpensive when compared with usual processes required by inorganics, such as vacuum vapour deposition.

The aim of this paper is to present a review of the great potential offered by the use of electroactive organic materials in devices capable of showing, in response to an electrical stimulation, tunable colour properties, manifested either as a change of intrinsic coloration or as an emission of coloured light. For this purpose, most relevant materials, devices, principles of operation and applications related to this theme will be reviewed here. The analysis will concern those effects which have a prevalent role in the electrical stimulation of colours: electrochromism, electroluminescence and lasing. Devices exploiting such effects are respectively known as electrochromics, light emitting diodes (LEDs) and light amplifiers by stimulated emission of radiation (LASERs).

In their organic implementation, each of these devices basically consist of an electrochemical cell which include an ion-conducting electrolyte medium (either liquid or solid) and one or more organic materials, whose response to supplied electrical energy accounts, according to different principles, for a variation of their electrical/optical properties, resulting in generation of colour.

As will be shown in the next sections, the predominant class of organic electroactive materials employed in these devices consists of  $\pi$ -conjugated polymers, one of the most outstanding families of EAPs. These polymers present  $\pi$ -electron delocalisation, arising from conjugated double bonds in the polymer backbone. They are usually termed also *conducting polymers*, since they can show very high electrical conductivity in doped states (*p*-doping or *n*-doping, if positive or negative charges are respectively injected), although being insulators when undoped (neutral state) [9–11]. Since the first report on their discovery, which dates back to 1977 [12], the great progress in research and applications of conducting polymers has caused their fathers Heeger, MacDiarmid and Shirakawa to be honoured with the Nobel Prize in Chemistry in 2000 [9–11]. It is well known today that, beyond the conducting and insulating states, these materials can also show a semiconducting one. Such different electrical properties are basically determined by the degree of  $\pi$ -orbital overlapping of nearby molecules, which is responsible for the actual ability of the material to transport electric charges (electrons and holes). In order to develop the different types of devices listed above, conducting and semiconducting properties of  $\pi$ -conjugated polymers and other organic electroactive materials (described in the following sections) are separately exploited.

Electrolytes typically used in these devices, as in any other electrochemical cell, belong to four main classes: aqueous electrolytes, organic liquid electrolytes, ionic liquids and solid polymer electrolytes. Aqueous and organic liquid electrolytes are very common. The first ones encompass both acids (e.g.  $\text{H}_2\text{SO}_4$ ) and bases (e.g. KOH), while the second include representatives like propylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC) or diethyl carbonate (DEC), frequently added to metal salts, such as lithium perchlorate ( $\text{LiClO}_4$ ), sodium perchlorate ( $\text{NaClO}_4$ ) or lithium hexafluorophosphate ( $\text{LiPF}_6$ ), in order to achieve improved electrochemical properties. The third class of liquid electrolytes is represented by the so-called *ionic liquids*, such as ethyl ammonium nitrate ( $[\text{EtNH}_3][\text{NO}_3]$ ), 1-butyl-3-methylimidazolium tetrafluoroborate ( $[\text{BMIM}][\text{BF}_4]$ ) or 1-butyl-3-methylimidazolium hexafluorophosphate ( $[\text{BMIM}][\text{PF}_6]$ ). They are room-temperature fluid salts made of organic cations and inorganic anions [13,14], whose adoption can result in improved lifetime and response speed of diverse types of electrochemical devices, as recently reported for electrochromics and actuators [14]. In contrast to such liquid-state ion conductors, requirements for all-solid-state cells are best met by solid polymer electrolytes (SPEs) (or polymer ionics) [15,16]. Most SPEs used can be classified as follows: (1) polymer or gel matrixes swollen with liquid electrolyte solutions (e.g. EC/polyacrylonitrile (PAN)/sodium perchlorate ( $\text{NaClO}_4$ )); (2) single-ion systems in which only one ionic species is mobile within a polymer matrix (e.g. perfluorosulfonate ionomer Nafion<sup>®</sup>); (3) solvent-free ion-coupled systems consisting of ion-solvating polymers mixed with salts, so that cations and ions become mobile within the polymer network (e.g. poly(ethylene oxide) (PEO) mixed with salts). In order to couple the attractive performances of ionic liquids with the advantages of a solid-state medium, composite electrolytes have been proposed, consisting of ionic liquids mixed with polymer or gel matrixes [17,18]. However, owing to the very recent use of ionic liquids as high-performance electrolytes (although known for many decades), such polymer/ionic-liquid composites have not been largely studied to date.

The following sections separately consider organic electrochromism, electroluminescence and lasing, in order to analyse their relevance for electrical stimulation of colours in organic materials.

## 2. Organic electrochromic devices

A material is usually said to be *electrochromic* if it shows reversible colour changes when a potential difference is applied across it. More properly, the electrochromic effect is defined as a visible and

Table 1  
Most used electrochromic organic and inorganic materials

Organics (EAPs and macromoleculars)	Inorganics
Conducting polymers: Polythiophene and its derivatives: e.g. Polythiophene (PT) e.g. Poly(3,4-ethylene dioxythiophene) (PEDOT) e.g. Poly(3-methyl thiophene) (PMT) e.g. Poly(3-hexyl thiophene) (PHT) e.g. Poly(3-alkyl thiophene) (PAT) e.g. Poly(3,4-propylenedioxythiophene) (PProDOT) Poly(3,3-dimethyl-3,4-dihydro-2H-thieno(3,4-b)(1,4)dioxepine) (PProDOT-(CH <sub>3</sub> ) <sub>2</sub> ) Poly(3,4-ethylenedioxyppyrrrole) (PEDOP) Poly(3,4-(2,2-dimethylpropylenedioxy)-pyrrole) (PProDOP-(CH <sub>3</sub> ) <sub>2</sub> ) Poly(3,6-bis(3,4-ethylenedioxy)thienyl)-N-methylcarbazole) (PBEDOT-NMeCz) Poly(2-(3,4-ethylenedioxy)thienyl-(biphenyl)) (PBEDOT-BP) Polyaniline (PAni) Polypyrrrole (PPy)	Transition metal oxides: e.g. WO <sub>3</sub> e.g. IrO <sub>2</sub> e.g. TiO <sub>2</sub> e.g. Nb <sub>2</sub> O <sub>5</sub> e.g. Nb <sub>2</sub> O <sub>5</sub> :Li <sup>+</sup> e.g. Nb <sub>2</sub> O <sub>5</sub> -TiO <sub>2</sub> e.g. MoO <sub>3</sub> e.g. V <sub>2</sub> O <sub>5</sub> Iron hexacyanoferrates ('Prussian colours' family): e.g. Prussian blue: [Fe <sup>III</sup> Fe <sup>II</sup> (CN) <sub>6</sub> ] <sup>-</sup> e.g. Prussian green: [Fe <sup>III</sup> {Fe <sup>III</sup> (CN) <sub>6</sub> } <sub>2</sub> {Fe <sup>II</sup> (CN) <sub>6</sub> }] <sup>-</sup> e.g. Prussian white: [Fe <sup>II</sup> Fe <sup>II</sup> (CN) <sub>6</sub> ] <sup>2-</sup> e.g. Prussian brown: [Fe <sup>III</sup> Fe <sup>III</sup> (CN) <sub>6</sub> ] <sub>2</sub>
Viologens: 1,1'-Disubstituted-4,4'-bipyridinium salts Metallopolymers Metallophthalocyanines (M-Pc): e.g. Lu(Pc) <sub>2</sub>	

reversible variation of optical properties, namely light transmittance and/or reflectance, shown by a material upon its electrochemical oxidation/reduction.

The particular properties of transmission or reflection of light account for the peculiar colour of an electrochromic material. Colour changes typically range between a transparent (*bleached*) state and one or two coloured states, corresponding to different red-ox conditions. In the case of a material's capability of manifesting several colours, it is termed *polyelectrochromic*.

Historically, following the first report on electrochromism by Deb in 1969 [19], transition metal oxides, and particularly tungsten trioxide (WO<sub>3</sub>), were the first inorganic materials in which the electrochromic effect was observed and reported.

Currently, this effect is being studied not only with inorganic materials [20–22] but also, and largely, in organic compounds such as conjugated polymers, viologens, metallo-polymers and metallo-phthalocyanines, as reported in Table 1 [21,23]. In fact, as will be shown in this section, organic electrochromic materials offer several advantages with respect to inorganics, not only in terms of flexibility, ease of processing and low cost, but also with respect to both 'tailorability' and efficiency of coloration.

The structure of a classical electrochromic device is that of a typical multilayer electrochemical cell, represented in Fig. 1. It consists of up to seven layers of materials, transparent to visible light. The electrochromic material is coupled to an ion conductor (solid or liquid electrolyte) and an ion storage layer; these three

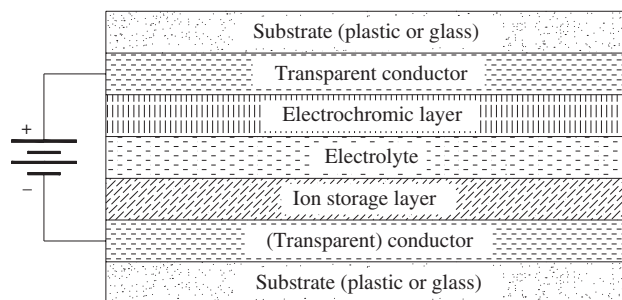


Fig. 1. Classical seven-layer structure of an electrochromic device.

optically transparent layers are sandwiched between two conductors, at least one of which must be transparent too (typically made of indium tin oxide (ITO)). The resulting five layers are protected by two transparent plastic or glass substrates. The electrochromic layer can be coupled to either the cell anode (as in Fig. 1) or cathode. In the two cases it is respectively said to be an anodically or cathodically colouring material, i.e. it shows colour variation when it is oxidised or reduced. Alternatively, two electrochromic species can be present in two symmetrically arranged layers; for such a case, cathodic and anodic coloration processes are simultaneously driven.

By applying a voltage difference (typically 1–5 V) to the cell, the electrochromic material is oxidised or reduced, depending on the voltage polarity. The electrochromic effect is induced by such electrochemical red-ox processes experienced by the active material. In particular, following its oxidation (reduction), the

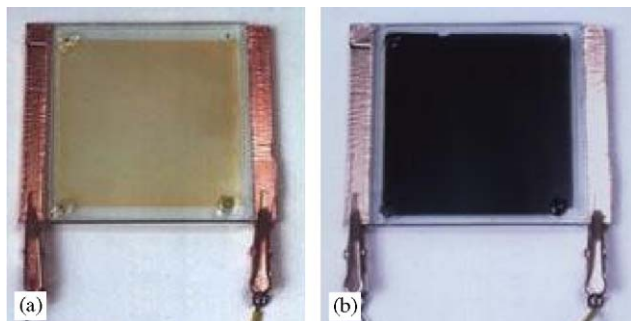


Fig. 2. Colour switching of an electrochromic device from its bleached (a) to its coloured state (b) (adapted from [25]).

material experiences an insertion of counter anions (cations), flowing into it from the ion storage layer through the ion-conducting electrolyte; such ions carry out an anodic (cathodic) doping of the material, in order to balance its ejected (injected) electric charge. As a result, the electrochromic effect arises from the occurring modification of electronic properties of the material (in particular its band gap [24]), correlated to a variation of its optical properties (e.g. absorption bands) and, then, its colour (Fig. 2). As an example, in the case of a  $\pi$ -conjugated conducting polymer being used as an anodically colouring material, its oxidation causes an intake of counter anions in the polymer network, in order to restore electroneutrality. The value of the energy gap between the valence band (i.e. the highest band occupied by  $\pi$  electrons) and the conduction band (i.e. the lowest unoccupied band) is responsible for the optical properties of the material and, therefore, of its colour [2,23].

In terms of light propagation, the functioning of an electrochromic device can be classified among the following three types: transmission/absorption (both electrodes are transparent), specular reflection/absorption (one electrode is transparent, the other reflective) and diffuse scattering/absorption (at least one electrode is transparent) [2,22]. The structure of the device in all such cases is basically the one presented above, even though slight differences can occur. In particular, in addition to the classical battery-like configuration sketched in Fig. 1, two alternatives are possible: the first one is termed *solution configuration* and consists of an electrochemical cell having the electrochromic material (or both, in case of two) dissolved in a liquid or gel electrolyte; the second one is called *hybrid configuration* and is necessarily related to the presence of two electrochromic species, only one of which is dissolved in a liquid or gel electrolyte [26].

A simplified structure was recently proposed by Mecerreyes et al. [27]. They proposed a five-layer device, where each transparent conducting layer of the classical configuration is eliminated, its function being exerted by

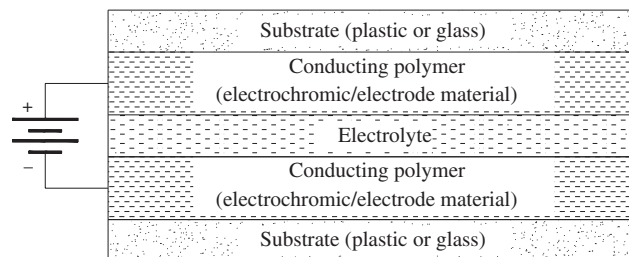


Fig. 3. Five-layer structure of an electrochromic device.

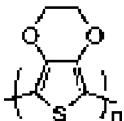


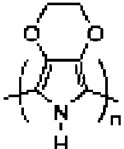
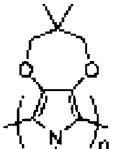
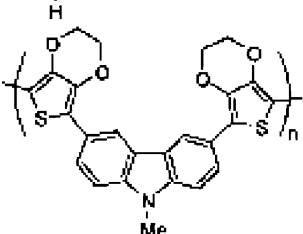
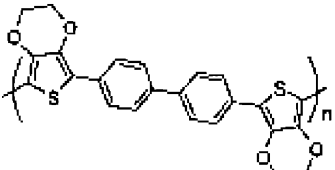
a layer of conducting polymer, which actually acts as both electrochromic and electrode material (Fig. 3). Such a configuration was successfully tested by using a tetrahydrofuran solution of a poly(ethylene oxide-lithium tri-flate) ( $\text{PEO} + \text{CF}_3\text{SO}_3\text{Li}$ ) as polymer electrolyte, whereas poly(3,4-ethylene dioxythiophene) (PEDOT) was employed as an electroactive polymer with electrochromic/conductive properties.

PEDOT is a widely used conducting polymer suitable for several types of applications [28]. This polymer and its alkyl derivatives show typically cathodically colouring electrochromic properties. Therefore, they can be used also in combination with anodically colouring materials (most of conducting polymers), in order to develop dual polymer devices [24,29]. Nevertheless, a new bipropylendioxythiophene (poly(spiroBiProDOT)) has been recently shown to have dual cathodically and anodically colouring properties, manifesting three different colours in the oxidised, neutral and reduced states [21,30]. PEDOT presents a transparent blue colour in the oxidised state, compared with a dark blue when it is neutral, as shown in Table 2 [23,31]. This table reports the molecular structure and colours (in doped and neutral states) of several organic materials studied by Thompson and co-workers in electrochromic organic cells with high coloration efficiency [31].

Polypyrrole (PPy) and polyaniline (PAni) are two more examples of conducting polymers subject to wide investigations (not only for electrochromic applications). Ppy (Fig. 4a) shows a blue/violet colour in oxidised state, while the neutral state (undoped) is yellow/green [21,23,32]; nevertheless, PPy typically presents low cycle lifetime, discouraging its use for reliable devices at the moment [23]. PAni (Fig. 4b) is polyelectrochromic, since in various red-ox states it can show several colours, such as yellow (leucoemeraldine), green (emeraldine salt), blue (emeraldine base) and black (pernigraniline) [21,23].

The use of conjugated polymers in electrochromic devices permits a fine tuning of colours. This represents one of the greatest advantages of choosing organic compounds rather than inorganic materials. In fact, colour control in electrochromic polymers can be easily

Table 2  
Chemical structure and colours of several high-performance electrochromic polymers

Electrochromic polymer <sup>a</sup>	Chemical structure	Colour (approximate indication)	
		Undoped state	Doped state
PEDOT		Dark blue	Transparent light blue
PMT		Bordeaux-red	Light blue
PProDOT-(CH <sub>3</sub> ) <sub>2</sub>		Transparent light blue	Blue
PEDOP		Pink	Transparent light blue
PProDOP-(CH <sub>3</sub> ) <sub>2</sub>		Red-orange	Transparent light blue
PBEDOT-NMeCz		Yellow	Blue
PBEDOT-BP		Brown	Black

<sup>a</sup>See Table 1 for nomenclature.

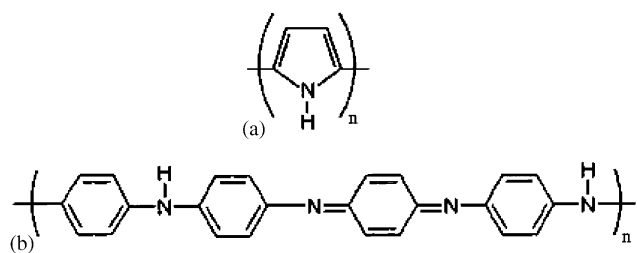


Fig. 4. Molecular structure of polypyrrole (a) and polyaniline (b).

achieved by following several strategies, such as group substitution (monomer functionalisation) aimed to modify the polymer conjugation lengths, copolymerisa-

tion of distinct monomers, as well as formation of blends, laminates or composites [31,33–35].

One of the most relevant examples concerns polythiophene (whose colour is red or blue in undoped or oxidised states, respectively [21]): the large family of polythiophene-derived polymers (some representatives are included in Table 2) comprises materials whose widely investigated electrochromic properties [36] are usually tailored by careful selection of thiophene monomers, permitting a broad range of colours, such as pale blue, blue and violet in oxidised doped states, with purple, yellow, red and orange in the neutral state [21,23,32].



The composite approach for colour control is frequently adopted in order to obtain polyelectrochromic devices, by combining materials with different colour regions [31,33,35]. Moreover, composites between organic and inorganic materials are also used, not only for multicolour devices but also to decrease driving potentials; several examples have been reported, such as the combination of PANi with the inorganic complex  $[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6]^-$  (commonly termed ‘Prussian blue’) leading to blue–green electrochromic devices [21,32,37–39].

The strategies adopted for conjugated polymers in order to obtain colour control are also used in other organic compounds, such as viologens (Fig 5a). For instance, intense colours shown by reduced viologens can be modulated by opportune selection of suitable substituent groups R and R'. In particular, blue/violet or green colours can be shown by using, respectively, alkyl or aryl groups [21,23].

In addition to viologens, metallo-phthalocyanines form another class of organic non-polymeric materials studied for electrochromic devices. Their molecules have a metal ion (M) which can be located either at the centre of a phthalocyanine (Pc) ring, as represented in Fig. 5b, or between a couple of molecular rings forming a sandwich-like structure. These materials can show electrochromic and even polyelectrochromic properties.

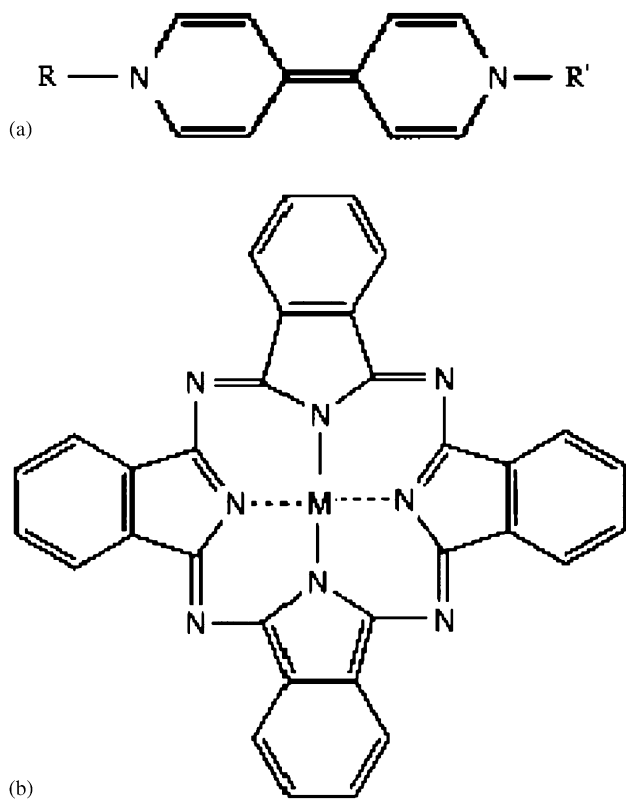


Fig. 5. Chemical structure of viologens (a) and metallo-phthalocyanines (b).

As an example, the green colour shown by neutral  $\text{Lu}(\text{Pc})_2$  can be converted to blue upon reduction or to yellow on oxidation [21,23].

The use of organic materials in electrochromic devices has been limited, for many years, as compared with inorganics, owing to reduced values of crucial figures of merit such as stability/lifetime, response speed and coloration efficiency shown by several devices. As a rule of thumb, one should take into account coloration switching times of the order of 1–10 s [21].

However, more recently considerable improvements have been made and, in certain cases, organics have demonstrated better performance than inorganics. As an example, we mention here the successful use of ionic liquids as electrolytes for organic devices, enabling a remarkable increase of both lifetime and switching speeds. In particular, an electrochromic 7-pixel numeric display built with PANi as anodically colouring polymer and PEDOT with poly(3-octylthiophene) (POT) as cathodically colouring polymer demonstrated a 100 ms response time and stability for  $10^6$  cycles when operated in  $[\text{BMIM}][\text{BF}_4]$  ionic liquid between  $-1.5$  (bleached state) and  $1.5$  V (coloured state) [14]. Reduced switching times have also been obtained with different approaches, such as the use of a viologen-modified nanostructured  $\text{TiO}_2$  film as electrochromic material which has shown response times lower than 50 ms [40].

Moreover, it has been reported that driving viologens-based electrochromic devices with square-wave pulsed potentials can increase their response speed in terms of colour formation [41]. As an observation, it is interesting to note here that such an approach based on the application of unusually pulsed and relatively high voltages, is gaining in the last few years an increasing relevance in several fields, not just the electrochromic one. In fact, this technique has been demonstrated to be useful in improving response speeds of systems which, although having completely different functionalities, share a structure based on an electrochemical cell, implemented with EAPs. As examples, we can merely mention recent successful improvements on the deformation speed of electro-(chemo)-mechanical actuators made of conducting polymers and carbon nanotubes [42,43].

It is relevant to stress that with respect to the best performing inorganic electrochromic material, namely  $\text{WO}_3$ , certain conducting polymers, such as PANi, PMT, PEDOT, as well as derivatives of PProDOT and PBEDOT (Table 1), exhibit today higher efficiency of coloration (electrochromic efficiency). In particular, poly(1,4-bis(2-(3',4'-ethylenedioxy)thienyl)-2-methoxy-5-2''-ethylhexyloxybenzene) (P(BEDOT-MEHB)) has very recently shown an efficiency of  $680 \text{ cm}^2/\text{C}$  at a wavelength of 535 nm, this value being one order of magnitude higher than for  $\text{WO}_3$  [44].

Such superiority in terms of coloration efficiency of EAPs, combined with their unique coloration tunability and reported improved lifetime and response speed, give a concise explanation for the growing interest shown by the research community in these materials for electrochromic applications. From this point of view and in consideration of the advantages for several applications deriving from their availability, all-plastic devices represent one of the longed-for goals in the electrochromic field. Despite relevant contributions [45,46], no examples are commercially available so far. This is due to the challenging nature of several problems which still need to be solved, such as the quality of transparent conductor layers on flexible substrates. However, remarkable research investigations are currently in progress. Recently, Argun and co-workers have proposed all-polymer electrochromic devices by using poly(3,4-ethylenedioxythiophene)-poly(styrene sulpho-nate) (PEDOT-PSS) as a transparent conductive layer [47].

Electrochromic viologens and other organic compounds have found applications in already commercial products, such as glare attenuation devices for car rear-view mirrors [23,48]. These systems are designed as a support for drivers in order to reduce mirror glares due to following vehicles. As an example, Gentex Corporation commercialises an electrochromic technology for auto-dimming rear-view mirrors [49]. The core of the system consists of a solution-phase device, containing a solvent with two electrochromic species (one of which is based on a viologen) used for dual coloration (cathodic and anodic); the solution is sandwiched between two glass layers, one coated with a transparent conductor and the other with a reflective one [21]. A forward-facing sensor recognises low ambient lighting and activates the system, while a rearward-facing sensor detects glare from vehicles and triggers a voltage supply to the electrochromic device (working in specular reflection/absorption mode) in order to modify the mirror coloration for a suitable glare attenuation [21,32,49], as presented in Fig. 6.

Glare attenuation devices based on electrochromics will also be employed in other systems, such as aircrafts, for the development of smart visors and windows for pilots and passengers [48]. Moreover, smart windows which exploit the electrochromic effect are starting to be used in buildings in order to reduce energy consumption by regulation of lighting and heating [20,48]. Such so-called *electrochromic windows*, in fact, operate an electrically driven control of solar gains (both infrared and visible components), through transitions ranging from transmissive to non-transmissive states. Such a control is aimed at a regulation of interior light and temperature, depending on weather conditions. They permit a comfortable day lighting and a reduction of



Fig. 6. Electrochromic autodimming car rear-view mirrors (from [49]).



Fig. 7. Electrochromic windows installed in a test room (adapted from [50]).

heat losses or overheating. Fig. 7 shows an office room with electrochromic windows.

One of the widest markets in which organic-based devices with electrically responsive colour properties can express their high potential is certainly represented by that of displays. The demand of flat, thin, light-weight, low-cost and in some cases flexible displays has continuously increased in the last few years, pushed by the development of new portable electronic instruments for communication and information diffusion/handling, such as multifunctional cell phones, palmtops, laptops, digital cameras and personal data assistants. Systems for home entertainment uses also require new large-area flat-panel displays. Full-colour devices based on organic



Fig. 8. Electrochromic display by Ntera Ltd made of a nanostructured metal oxide film with a layer of viologen.

materials show great potentialities in such applications. They can be easily fabricated onto flexible plastic substrates, even with large areas, enabling the use of fabrication processes with reduced costs and the realisation of products with low weights, low-voltage operation, high flexibility, wide viewing angles, good optical contrast and large areas. In this context, displays based on organic electrochromics are under development today and some simple examples, such as alphanumeric and grey-tone image displays (with comparable or superior performance to liquid-crystal displays), have already reached the market (Fig. 8). However, the strongest potential in this market is shown by electroluminescent devices, rather than electrochromics, as presented in the next section.

For the sake of completeness of an overview on the applications of electrochromism, we finally mention their suitable use for so-called *electronic paper* displays. In this technology, sometimes also referred as *electrochromic printing*, an electrochromic dye is embedded into a sheet of paper, covered by a couple of transparent electrodes. Following the application of a voltage difference, the dye darkens. It also remains dark when the voltage is removed. On the contrary, by supplying an opposite voltage difference, the dye lightens and the structure appears again paper-white. Accordingly, such an effect may be exploited for futuristic electronic newspapers, books or wallpapers, capable of a dynamic display of information [51].

### 3. Organic electroluminescent devices

Electroluminescence (conversion of electrical energy into light energy) can be achieved in materials showing semiconducting electrical properties. Organic semicon-

ductors, mainly  $\pi$ -electron oligomers and polymers [3,5,9–11], have found several applications as electronic and optoelectronic flexible devices [1–5]. In this section their use as electroluminescent materials will be discussed.

The first descriptions of electroluminescence in gallium arsenide (GaAs) p–n junctions date back to 1962 [52], while the first study on electroluminescent properties of a small organic molecule (anthracene) was described in 1963 [53]. Organic electroluminescent devices, known also as organic light emitting diodes (OLEDs), consist of components capable of emitting light in response to an electrical input. They are usually assembled as multilayer structures, where organic emitters are embedded between thin electrodes, one of which is made of a conducting transparent material coupled to a plastic or glass substrate (Fig. 9).

The basic principle of operation of such a device can be described as follows. When a potential difference (typically of the order of 1–10 V) is applied between the electrode couple, charge carriers are injected by the electrodes (electrons from the cathode and holes from the anode) and transported towards the active organic layer.

This material is responsible for light emission, as a consequence of the recombination of the two species of charge carriers and the related formation of an excited molecular state (exciton), whose following relaxation to previous ground state triggers luminescence. Although examples of devices fabricated with only one active layer have been reported, two additional organic conducting layers are frequently inserted to help transport of

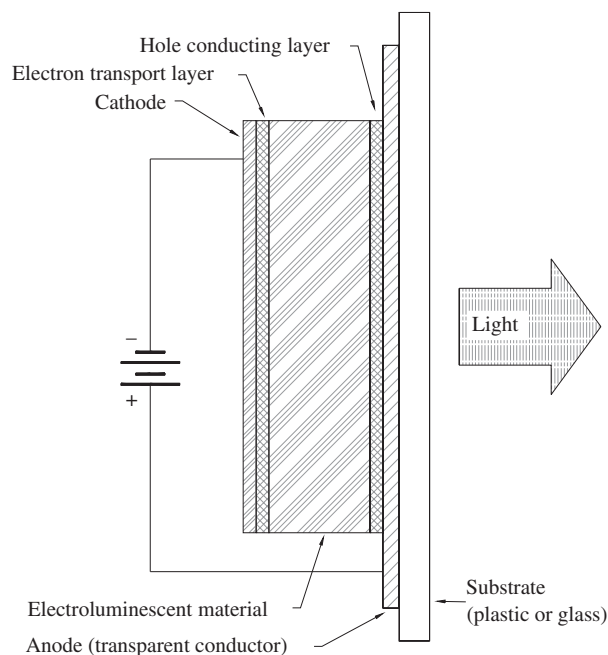


Fig. 9. Classical structure of an OLED.



charges. In Fig. 9, two layers for transport of hole- and electron-type charges are inserted between the emitting material and, respectively, the anode and the cathode.

Transparent metal electrodes typically consist of tin-doped indium oxide evaporated thin films, which permit high transmittance of visible light as well as low electrical resistivity.

The emitting layer can be made of several types of organic semiconductors, enabling a selection of different emission wavelengths in the visible spectrum [54,55]. Poly(*p*-phenylene vinylene) (PPV), poly(2-methoxy-5-(2'-ethyl-hexoxy)-*p*-phenylenevinylene) (MEH-PPV) and polyfluorenes (PFs) are very common electroluminescent polymers capable of showing, respectively, green, orange-red and blue colours. Table 3 provides a non-exhaustive summary of the most frequently used organic and inorganic electroluminescent materials. Molecular structures of the principal organic representatives are reported in Fig. 10.

Interestingly, most of organic materials used in OLEDs show both electro- and photo-luminescence, as presented in Fig. 11. The colour of the electroluminescent emission of  $\pi$ -conjugated polymers depends upon their conjugation length. In particular, short-range conjugations are responsible for blue-shifted emissions, whereas red-shifted colours are ascribable to long-range conjugations [55]. Therefore, as for electrochromic polymers, a high degree of colour tailorability can be achieved by synthesising electroluminescent polymers with specific conjugation lengths.

This is usually achieved in several ways, such as block copolymerisations and addition of different substituent groups to the repeating units of the polymer backbone [54,55]. Copolymerisation is also frequently used as a means to improve electroluminescence efficiency [57]. Moreover, in a manner similar to electrochromics,

colour selection and improved brightness are also achieved through the development of suitable composite materials with either inorganics or small organic molecules [4,5,7,58,59]. Small molecule OLEDs (or SMOLEDs) usually adopt organic emissive molecules having molecular weights not higher than several hundred Daltons. Typical representatives of such a class of materials are anthracene, arenes or pentacenes, which frequently are employed in combination with species including transition metal atoms [60]. Improved efficiencies can be obtained with the insertion of electrophosphorescent compounds in the organic emitting layer; by this method, power efficiencies up to 30–40 lm/W with about 4 V of driving voltage have been reported [7,61,62].

An alternative to the OLED structure of Fig. 9 was reported by Pei et al. [64,65]. They proposed the so-called *light-emitting electrochemical cell* (LEC), consisting of two transparent electrodes (typically made of ITO), which include a blend of an electroluminescent polymer with a polymer electrolyte. Following the application of a potential difference between the electrodes, polymer oxidation and reduction take place at anode and cathode, respectively, with related injection of *p*- and *n*-type charge carriers (holes and electrons); they are electrically balanced by anions and cations diffusion inside the electrolyte/electroluminescent medium, where they also recombine with consequent light emission. PEO mixed with lithium salts is frequently used as solid polymer electrolyte in these devices [2].

The poorer semiconducting performances demonstrated by state-of-the-art organic materials, in comparison with inorganics, are due to certain fundamental parameters. These include charge injection, charge carrier mobility and electron–hole recombination, and

Table 3  
Most used electroluminescent organic and inorganic materials

Organics (EAPs and macromoleculars)	Inorganics
Poly( <i>p</i> -phenylene vinylene) (PPV)	Aluminium gallium indium phosphide (AlGaInP)
Poly(2-methoxy-5-(2'-ethyl-hexoxy)- <i>p</i> -phenylenevinylene) (MEH-PPV)	Aluminium gallium arsenide (AlGaAs)
Poly(dialkoxo- <i>p</i> -phenylene vinylene) (PDAPV)	Aluminium indium gallium phosphide (AlInGaP)
Poly(paraphenylene) (PPP)	Gallium arsenide phosphide (GaAsP)
Polyfluorene (PF)	Gallium aluminum phosphide (GaAlP)
Poly(dialkyl fluorene) (PDAF)	Gallium arsenide (GaAs)
Polythiophenes (PT):	Gallium nitride (GaN)
e.g. Poly(3,4-ethylene dioxothiophene) (PEDOT) even doped with	Gallium phosphide (GaP)
Poly(styrenesulphonic acid) (PSS)	Germanium (Ge)
e.g. Poly(3-alkyl thiophene) (PAT)	Indium antimonide (InSb)
e.g. Poly(3-hexyl thiophene) (PHT)	Indium gallium nitride (InGaN)
Pentacene	Indium gallium aluminium phosphide (InGaAlP)
Polyaniline (PAni)	Silicon (Si)
	Silicon carbide (SiC)
	Zinc selenide (ZnSe)

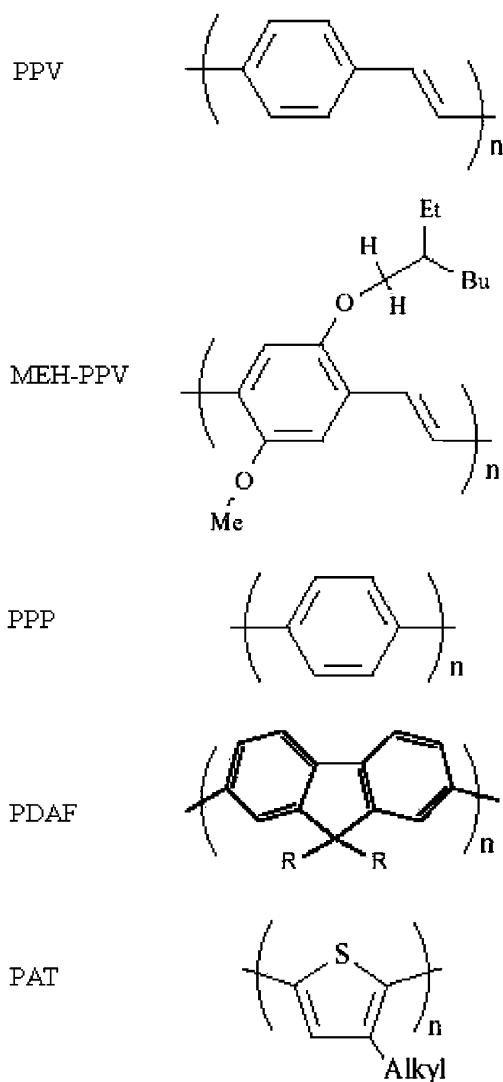


Fig. 10. Common electroluminescent polymers used in OLEDs (see Table 3 for nomenclature).



Fig. 11. Photoluminescence of liquid-phase organics (from [56]).

are responsible for the lower emission properties currently available [58]. However, OLEDs are studied for several applications, owing to their potential in other respects, such as mechanical flexibility, low cost and ease

of assembling in large-area panels employed as displays. Low driving voltages currently permit the achievement of considerably high brightness of emission. In particular, values of luminance (luminous intensity per unit area projected in a given direction) up to  $10^4$  cd/m<sup>2</sup> with potential differences of the order of 10 V have been reported [7,66]. Such performances are advantageously obtained from ultrathin, light and flexible structures, which can be adapted to several kinds of substrates [67].

Multicolour flat-panel displays are certainly one of the elected fields of application of the OLED technology [58,68,69]. More challenging anticipated applications are represented by flexible electronic paper displays and other supports for written/visual communication [70,71]. Despite the particular substrate on which they are realised, displays consist of matrixes of pixels made of LEDs. Each diode can be activated by means of high-current row-by-column electrodes (passive matrix displays) or through a dedicated nearby thin film transistor (TFT), interrogated via low-current row-by-column electrodes (active matrix displays). In multicolor displays, red, green and blue OLEDs are used as fundamental colour pixels in order to implement displays capable of covering the full colour spectrum. OLED-based systems present advantages in comparison to liquid crystal displays (LCDs), since they do not need back-lighting. This permits a lower thickness and a reduced weight, as well as a lower power consumption (estimated to require between 20% and 80% that of LCD systems [58]). Moreover, higher contrast, brightness and wider viewing angles (even in bright sunlight) are typical of OLEDs, in concomitance with superior response speeds [58].

The first commercial products with organic electroluminescent displays are currently being introduced into the market [58,63,72]. Kodak produces full-colour active matrix OLED displays, which have been incorporated in commercial products such as digital cameras (Fig. 12). Pioneer has launched automobile stereos with an OLED display (Fig. 13), while several producers of mobile phones have presented models which integrate such devices (Fig. 14). They have also been included in examples of wrist watches (Fig. 15) and electric shavers (Fig. 16).

Further substantial developments in such technologies based on organic electroluminescence are expected in the near future.

#### 4. Organic LASERS

For the sake of completeness of this overview of organic devices working as electrically driven 'colour generators', we briefly focus in this section on one of the last research frontiers having a potential future role in this field.



Fig. 12. (a) Kodak Nuvue Display AM550L. Characteristics: diagonal: 5.5 cm, weight: 8 g, peak luminance:  $120 \text{ cd/m}^2$ , power consumption: 400 mW. (b) Kodak EasyShare LS633 zoom digital camera equipped with the AM550L display (adapted from [73]).



Fig. 13. Pioneer organic display for car stereos (from [74]).

As a direct consequence of the electroluminescent properties shown by several semiconducting EAPs, these materials can be thought to be employable even in the development of LASERs. Such devices can be in fact basically conceived as an active material capable of amplifying light, coupled to a resonator. Light amplification is achieved through repeated stimulations (with related luminescence) induced in the active material by a light beam running inside it, alternately reflected backwards and forwards by the resonator. Therefore, semiconducting polymers with emission properties offer



Fig. 14. Pictures of some cell phones equipped with OLED displays: LG VX4600 (a), Motorola Timeport P8767 (b), Sanyo Sprint (c).



Fig. 15. Wrist watch with OLED display (adapted from [56]).

interesting potentialities in order to develop organic versions of these well-known instruments. Actually, conjugated polymers listed in Table 3 are also currently under investigation for lasing. A detailed summary of lasing properties of these and other polymers can be found in [75].

Several configurations have been proposed in order to implement efficient resonators in polymer LASERs. Most used consist of micro-cavities, micro-rings, micro-disks, micro-droplets and planar wave guides with distributed feedback (DFB) achieved by using corrugated substrates and 2D-gratings [8,75–77].



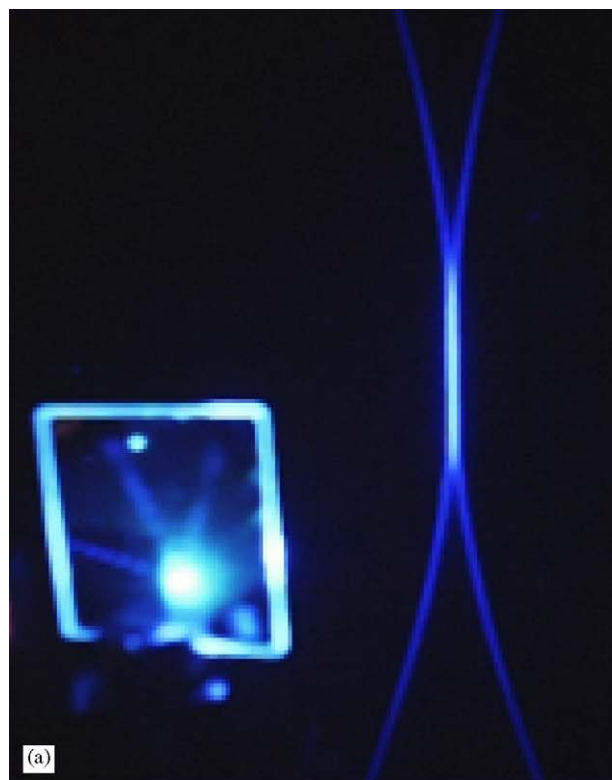


Fig. 16. Philips Philishave electric razor including an OLED display.

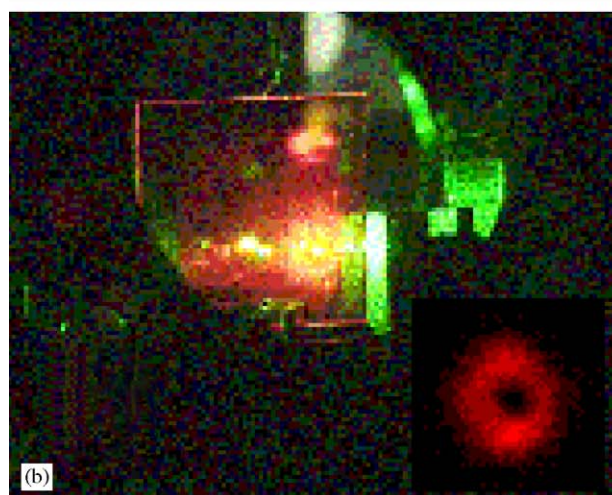
Prototype devices with emission wavelengths falling in the visible spectrum have been demonstrated. Fig. 17 reports two images obtained from high-performance semiconducting polymers. In general terms, polymer lasers offer attractive potential features, such as easy and cheap fabrication procedures, mechanical flexibility, separate absorption and emission bands, as well as broad emission spectra, which permit wavelength tuning. Emission bandwidths wider than 100 nm are typical of conjugated polymers.

With respect to the primary energy source, two types of LASERS can be recognised: those with electrical pumping and those with optical pumping [8]. The first type is driven by an electrical input applied to the emitting material, in order to trigger light generation, whose intensity is then progressively increased. This kind of operation is shared by the most diffused inorganic-based devices, which can be found in several commercial products, such as laser diodes of CD players.

The second type of LASERS is activated by an external light source, used to excite the emitting medium of the device. It is evident that an electrical source is the preferred choice for most applications. However, polymer LASERS developed so far belong to the optically pumped class only. This is basically due to the fact that electrical stimulations of currently available organics have not been able to induce emissions sufficiently high to reach the threshold energy for lasing. Therefore, all currently available polymer LASERS require driving by another laser source. Future improvements are expected



(a)



(b)

Fig. 17. Transverse and annular beam profile of, respectively, a polyfluorene surface-emitting DFB laser (a) and a MEH-PPV surface-emitting 2D DFB laser (b) (adapted from [78]).

from the development of emitting layers with superior charge carrier mobilities and with the use of pulsed sources.

## 5. Conclusions

This paper provides a review of fundamentals, latest developments and current applications of organic-based technologies exploiting electrochromism, electroluminescence and lasing as effects enabling the realisation of



devices with electrically responsive colour properties, in terms of either a variation of intrinsic colour or as an emission of coloured light. Colorations and emissions with high tailorability and suitable efficiency have been achieved today in electroactive polymers, so that several applications are currently approaching the market. Despite many challenging improvements still needed in order to increase competitiveness of devices based on electroactive polymers and other organic compounds, the great potentialities demonstrated so far by these materials enable their future advantageous employment in niche sectors where inorganics present intrinsic limitations.

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