Reviews

Electrochemiluminescence from Organic Emitters

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Electrically induced light emission from conjugated organic molecules in a condensed phase has constituted one of the most investigated phenomena in the recent past for a variety of reasons. The considerable development achieved in this field has been mainly based on the search of new configurations for luminescent devices such as flexible large area light-emitting diodes, and in the synthesis of improved light-emitting organic materials. In the present review a particular aspect of electrically induced light-emission phenomena from organic materials is considered, namely, organic electrochemiluminescence, which is the phenomenon of light emission from excited organic molecules generated upon occurrence of electrochemically driven redox reactions. Such processes can produce luminescence in the visible range if the resulting oxidized/reduced forms of the conjugated organic molecules form excited species capable of emitting photons within the energy range 1.5−3.5 eV. Electrochemiluminescence from organic emitters in a condensed phase has led to the creation of devices such as light-emitting electrochemical cells, whose realization was decisive in the development of effective light-emitting devices. In the present review the description of the phenomena at the basis of organic electrochemiluminescence is given together with the description of materials and devices configurations for light-emitting electrochemical cells.

Introduction

Electrochemical processes in conjugated organic materials can induce dramatic changes of their electronic properties as a consequence of the removal (addition) of electrons from (to) the HOMO (LUMO) of the organic compounds.[1] This is because conjugated organic compounds either in amorphous or crystalline state are characterized by the presence of a balanced electronic structure which can undergo severe modifications even upon small variations of the oxidation state of the molecular material.[2] Such a possibility offered by organic conjugated materials has been exploited for the realization of relevant electrochemically driven applications such as electrochemiluminescence (ECL),[3−7] photovoltaics,[8] or electrochromism.[9] Among the effects that electrochemically driven processes can produce in organic conjugated materials, light emission is certainly one of the most intriguing.[3,6a] This is not only because of the appearance of photons, or, from a strictly cognitive standpoint, for the production of electronically excited species during a reaction,[10] but also because of the considerable extent of control with which ECL can be generated in an electrochemical system. In fact, great accuracy can be achieved in the imposition of current and potential values in electrochemical cells with the available instrumentation.[11] The structural prerequisite of organic molecular materials for ECL production is the presence of a network of conjugated π-electrons with ionization energies in the interval 6.5−8.5 eV,[12] which gives rise to electronic transitions within the energy range 1.5−3.5 eV in either the ground or the excited state of the conjugated molecule.[13] Emissive transitions can be produced by the excited conjugated organic molecule in either the neutral or (less common) the charged state. Electrochemically driven redox reactions generate chemiluminescence essentially through the occurrence of charge recombination which produces electronically excited systems capable of emitting light upon relaxation.[14,15] Such a phenomenology points out the paramount importance of the charge transport properties in light-emitting molecular materials in terms of mobility of both kinds of electronic charge carriers, i.e., holes and electrons (or negative and positive polarons),[16] through the material since it is here considered ECL from conjugated molecules in a condensed phase.[3,17,18] Materials of potential interest for ECL generation must be then capable of being simultaneously both n-type and p-type conductors with electronic conductivity values not lower than, let us say, 0.1 S cm^{-1}, in order to be active materials for ECL.

In the following section an introductory part on the development of a particular class of light-emitting devices, i.e., light-emitting electrochemical cells (LECs),[3a,3b,3d,19] which generate ECL is presented. Successively, the ECL phenomena at the basis of light emission in LECs will be described and the mechanism which is operating in an organic LEC is compared with that one of an analogous light-emitting diode (LED).[14,20] Finally, a closure section will be dedicated to the review of organic materials whose light-emitting properties in LECs have been reported. In particular,

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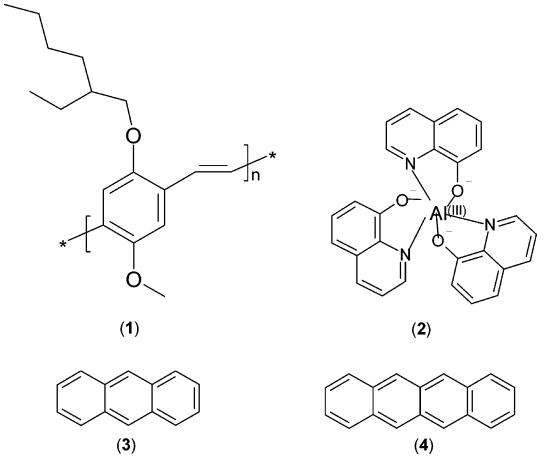


Figure 1. Structures of poly(2-methoxy-5-(2′-ethyl)hexyloxy-*p*-phenylenevinylene) (MEH−PPV) (**1**) (semiconducting polymer), tris(8-hydroxyquinolinate) aluminum (Alq_3) (**2**) (semiconducting complex), anthracene (**3**), and tetracene (**4**) (semiconducting molecules) for organic electroluminescence.

ECL[21] of organic emitters in the solid,[17] polymeric,[3] or dispersed states[18] will be considered, while ECL from organic emitters in solution[10,22,23] will not be covered in the present review.

Light-Emitting Devices Based on Organic Materials—LECs

In the past years particular attention has been devoted to the development and realization of organic light-emittig diodes (LEDs) for commercial large-area, thin, lightweight, flexible, high-density information full-color displays, backlights, and other lighting applications[24,25] as witnessed by the high number of patents (more than 5000 at the end of year 2004), related to the invention of devices based on organic LEDs at low manufacturing costs. Such an interest started in the late 1980s after the observation of electroluminescence (EL) from thin films of organic semiconducting polymers, e.g., MEH−PPV(**1**)[14e] in Figure 1, or complexes likeAlq_3(**2**)[26] in Figure 1, with thickness on the order of a few hundreds of nanometers, at relatively low values of applied voltages (<15 V), with a wide viewing angle and with external efficiencies on the order of a few lumens per Watt.[14u,27] The remarkable aspect of such a discovery was the relatively high efficiency of electrical charge conversion into emitted photons rather than its novelty. In fact, the phenomenon of EL from organic semiconductors was known since 1963 when Pope et al. reported on EL of 10−20 μm thick anthracene [(**3**) in Figure 1] single crystals and tetracene[(**4**) in Figure 1]-doped anthracene polarized at 400 V.[28]

During the years which separated the first discovery of organic EL in 1963 from the latest achievements of effective EL generation in organic materials at lower values of applied voltages, the development of increasingly efficient organic LEDs was more a consequence of the reduction of the thickness of the organic semiconductor layer rather than a significant improvement in the nature of the organic emitting material itself.[29] This was demonstrated by showing that the electric-field strength E and not the applied voltage V controls the electrical characteristics of an organic material-based diode.[30] In fact, for a series of LEDs based on poly(2-methoxy-5-(2′-ethyl)hexyloxy-*p*-phenylenevinylene) (MEH−PPV) with different thicknesses (range: 25−220 nm) and sandwiched between ITO anode and cathodes of different materials, it was found that the onset of current passage was in correspondence of a constant value of applied E ($=1 \times 10^8$ V m^{-1}) in the characteristics curves.[30] The maximum current density value achievable with such LED configurations was equal to 1.5 mA mm^{-2}.[30] In this perspective, initial organic LEDs development took place mainly for the efforts spent in the optimization of the configuration rather than in the synthesis of more efficient electroluminescent organic compounds.[31] On the other hand, the nature of the organic emitting material in LEDs was mostly considered in terms of the value of the energy gap between the level of lowest unoccupied molecular orbital (LUMO) and the level of the highest occupied molecular orbital (HOMO), which controls the wavelength of the emitted radiation (Figure 2).[32,33]

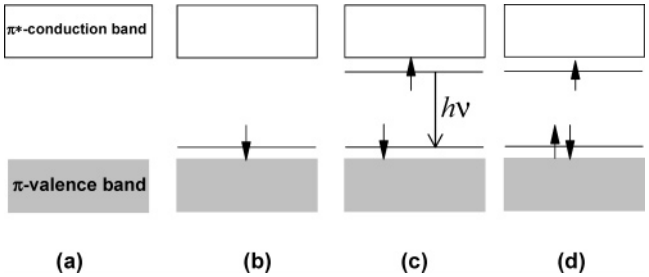


Figure 2. Evolution of the electronic band structure of an organic conjugated material in the condensed phase during the generation of electro- or electrochemically generated luminescence: (a) energy levels of the organic conjugated material in the electronically neutral state; (b)/(d) energy levels of the organic conjugated material in the positively/negatively charged state following electrochemical oxidation/reduction; (c) energy levels of the organic conjugated material in the emitting excited state generated upon annihilation of radical cations (from b) and radical anions (from d). The decay provoking luminescence in (c) is due to the organic emitter in a singlet excited state.

Emissive layers in LEDs made of conjugated polymers such as PPVs, polythiophenes, or polyparaphenylenes produce radiations with emission peak wavelengths λ_{ep} comprised in the range $400 < \lambda_{ep} < 750$ nm.[29b] Such variations of λ_{ep} are indicative of differences in the extent of electronic conjugation in the different emitting materials.

The prototype-configuration of organic LEDs based on semiconducting organic polymers such as MEH−PPV (**1**) (Figure 1) is a monolayered structure in which the active organic emitter MEH−PPV is sandwiched between two electrodes acting as hole and electron injectors (Figure 3).[14e]

A further refinement of the LED configuration in Figure 3 is represented by a similar multilayered structure in which additional hole- or electron-transporting layers separate the light-emitting layer respectively from the anode and the cathode in order to ameliorate charge injection and successive recombination inside the emissive layer.[32,34] Such organic LEDs are based exclusively on semiconducting materials, either emissive and/or charge-transporting, whose properties of electrical conductivity stem from the presence of mobile electronic, and not ionic, charge carriers. This implies some limitations in the combination of materials constituting charge-injecting electrodes, charge-transporting layers, and emissive layer in an organic LED.[30] In fact, the HOMO−LUMO gap of the emissive organic layer imposes the choice

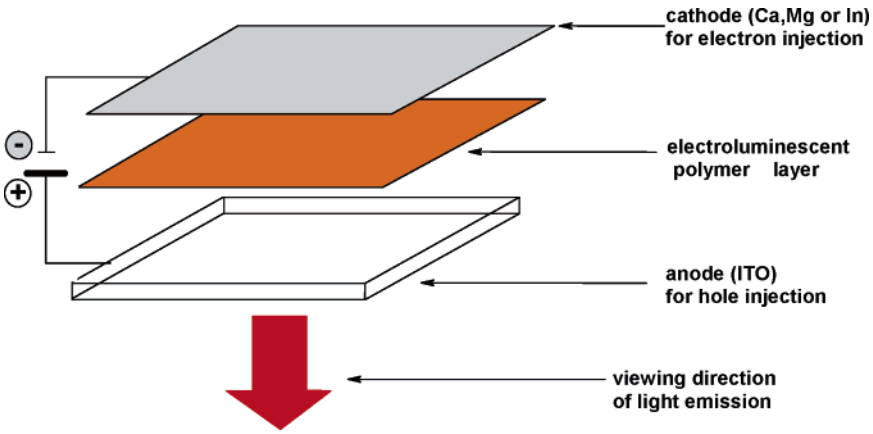


Figure 3. Sandwich configuration of an organic LED based on an active polymer like MEH−PPV (ITO is the transparent conductor indium tin oxide).

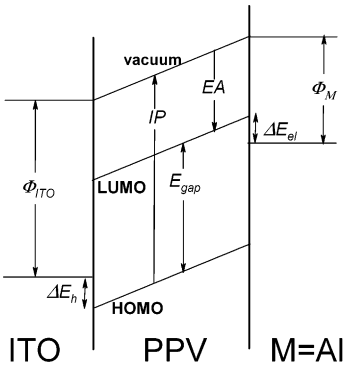


Figure 4. Qualitative diagram of the energy levels of a LED constituted by PPV as an organic emitting layer, and ITO and a low working function metal (Mg, Ca, or Al) as hole- and electron-injecting electrodes, respectively. $\Delta E_{h/el}$, $\Phi_{ITO/M}$, *IP*, *EA*, and E_{gap} are the energetic barriers for holes/electrons injection, the work function of ITO/metal electrode, the ionization potential of PPV, the electron affinity of PPV and the energy band gap of PPV, respectively.

of anodic and cathodic materials which must have work functions ϕ_{an} and ϕ_{cat} matching respectively the HOMO (π-band) and LUMO (π*-band) levels of the emitting material in the organic LED (Figure 4).[30b,35]

The major drawback of such a configuration is the need to develop new different cathodes and anodes for the optimization of light emission from an organic emitter at each single wavelength.[36] To overcome the problem of single-wavelength emission from fixed configuration of organic LEDs, a new different approach has been lately adopted through the assembling of light-emitting electrochemical cells (LECs) (Figure 5).[3a,3b]

These devices are electrochemical thin-layer cells[37] in which the light-emitting material is blended with ionic liquids[38] or polymeric[3a,3b,3e,39] electrolyte containing mobile charge-compensating ions. In a LEC the active organic species undergoes electrochemically driven redox processes to emit light. Different from LED, the ECL efficiency in LECs is scarcely affected by the electronic properties of the electrodic materials since ECL can be achieved even when charge-injecting electrodes are constituted by the same material.[3c,40] LECs can thus exhibit symmetrical current−voltage and light intensity−voltage characteristics curves (Figure 6).

In LEC light-emitting materials and electrodes do not present necessarily matching between HOMO and ϕ_{an} or between LUMO and ϕ_{cat} since charge injection at the electrodes is ionic space-charge-assisted and the turn-on for light emission is achieved at biases very close to the E_{gap} of the fluorescent polymer (Figure 7).[40g,40h]

As a consequence, LECs present the advantage of not requiring the use of cathodic materials with low ϕ_{cat}, which easily undergo oxygen degradation and provoke deleterious effects for the light-emitting device performance.[41]

In LECs the process of charge injection into the emissive layer corresponds to the electrochemical oxidation or reduction of the light-emitting material itself.[3a,3b,40b−d] As an electrochemical system, in a LEC the redox processes at the electrode/organic cromophore interface involve the formation of a double layer in which mobile ions from electrolyte are also participating with the replenishment of the outer Helmholtz plane.[19,42] This allows the occurrence of charge injection into the emissive layer of a LEC at generally lower thresholds with respect to a LED.[39e,43] Consequently, the turn-on voltage of a LEC is relatively independent of film thickness, since it usually approximates the optical gap of the light-emitting materials with no considerable increases due to ohmic drops.[17b] Another advantage of a LEC is the possibility of varying the emissive properties of the same organic cromophore with verification of multiple-wavelength emission if the electrolyte alters the intermolecular interactions between the emissive molecules.[44]

Phenomenology of Light Emission in LECs from Organic Molecules

Energy Considerations. Different from photoluminescence,[14n] ECL in semiconducting organic molecules is due to the radiative recombination (direct reaction) of two electronic charge carriers with opposite sign which have a sufficiently high difference of electronic energies.[19] To obtain ECL in the visible range (1.5−3.5 eV), the energy difference ΔE between the recombining entities has to be on the order of 40−70 kcal mol^{-1}.[45] From the energy standpoint, the difference between the potential values of oxidation (E_{ox}) and reduction (E_{red}) of the light-emitting material in a LEC has to be comprised in the corresponding energy range 1.5−3.5 eV if light emission in the UV−visible range must occur.[19,46] The electrochemical system does not reach immediately the thermodynamical equilibrium upon electrical polarization since the electrochemically injected charges

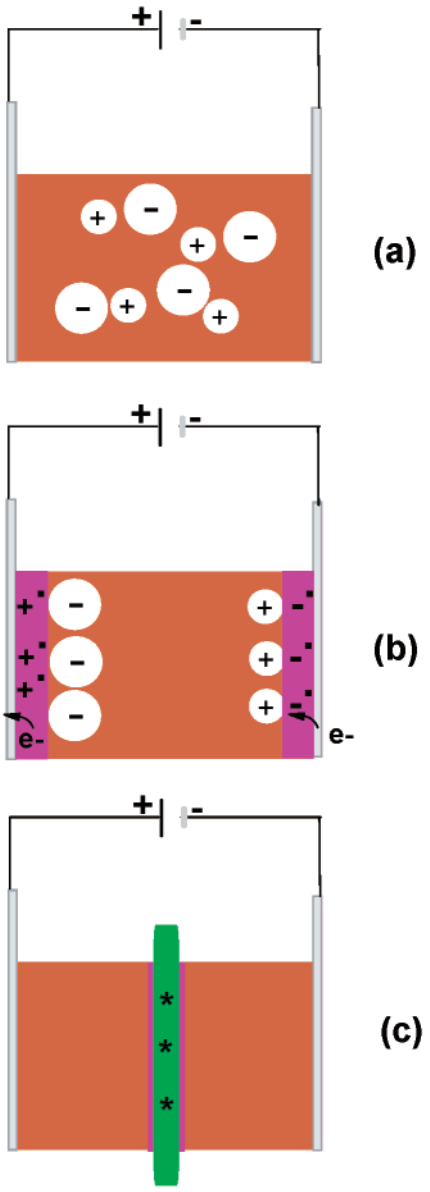


Figure 5. Schematic representation of the processes involved in the generation of chemiluminescence in a solid-state electrochemical cell with an organic conjugated polymer as luminescent redox species: (a) in the absence of cell polarization; (b) electrolysis of the conjugated polymer with formation of polymer radical cations and anions respectively at anode (left electrode) and cathode (right electrode); (c) migration of the radical cations and anions toward cathode and anode, respectively, with subsequent emissive recombination at the center of the solid-state electrochemical cell (indicated in green). White spheres in (a) and (b) represent the supporting electrolyte, whereas asterisks in (c) represent the emitted photons. Orange and violet colors indicate the conjugated polymer in the neutral and oxidized/reduced states, respectively. For sake of simplicity the supporting electrolyte is not depicted in (c).

require a diffusion/migration time to reach the distribution at equilibrium.[19,42] It is during the process of charges redistribution that excited state formation upon charge recombination takes place. Therefore, emission in LECs has to be considered as a transient phenomenon[14h] which is produced by the electrochemical system when achieving the status with minimum energy.[19,23c]

To be a LEC-active material, the necessary condition to fulfill is the verification of reversible oxidation (hole injection) and reduction (electron addition) of the material within the potential window of electrochemical stability of

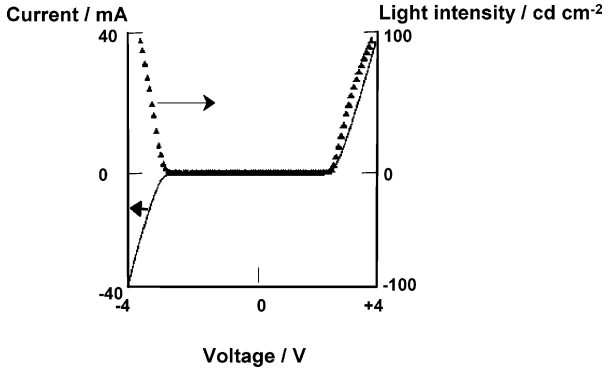


Figure 6. Current/light-voltage characteristics of a LEC in which the active layer is constituted by a blend of PPV with a polymer electrolyte (poly(ethylene oxide) + lithium salt). ITO and Al are the electrode materials (adapted from ref 3b).

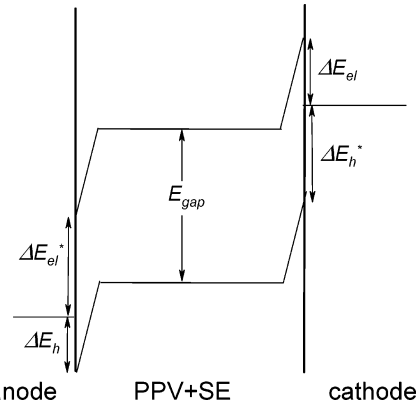


Figure 7. Schematic band diagram for a single-layer LEC. The active layer is made by an electrochemiluminescent conjugated polymer blended with an ionic conductor (supporting electrolyte). $\Delta E_{h/el}$ is the energetic barrier for holes/electrons injection, at the anode/cathode, respectively. $\Delta E_{h/el}$* is the energetic barrier for holes/electrons injection at the cathode/anode, respectively (adapted from ref 40g).

the LEC electrolyte. This would prevent uneffective charge injection through the LEC due to the occurrence of redox processes involving the sole electrolyte.[40b,40c,47]

A possible source of energy dissipation in LECs is represented by the ohmic drop associated with the electrical resistance of the electrolyte,[48] which brings about the waste of a portion of the applied potential for the activation of charge motion through the LEC electrolyte.[42,49]

Charge Transport Issues in Organic LECs. In a LEC radiative recombination is made possible by the migration and, to a lesser extent, by diffusion of the diverse mobile charged species from the parent electrode toward a zone of charge neutralization whose distance from the charge-injecting electrodes can vary depending on the nature of the light-emitting materials and LEC configurations.[3a,3m,40b−d,46,50] An important class of materials for organic LECs is constituted by semiconducting polymers.[51] In particular, PPV derivatives, e.g. MEH−PPV (Figure 1),[3] poly[2,5-bis-(triethoxymethoxy)-1,4-phenylene vinylene] (BTEM-PPV),[40c] poly[2,3-dibuthoxy-1,4-phenylene vinylene] (DB−PPV),[40c] poly(alkylthiophene),[40d] or poly(dialkylfluorene) (PF),[52] have been demonstrated as emissive materials in LECs. The electronic structure of these polymers is characterized by the presence of an extended system of π-electrons from occupied p_z orbitals of C atoms, which is delocalized over a stable polymeric backbone held by σ bonds. The occurrence of

conjugation gives brings about a general lowering of the electronic energy and gives rise to an electronic band structure (Figure 2).[1f,13a,53] Each polymeric chain has to be considered as a series of conjugated segments separated by structural distortions which do not allow the full electronic conjugation over the entire polymer backbone. As a consequence, the conjugated segments of a polymeric chain behave as electronically separate entities whose energies are distributed over a range of values which are associated with a distribution of electronic states.[54] These features do not allow the univocal identification of the actual charge carriers in light-emitting polymers in terms of effective mass, mobility, or charge density since a distribution of values for the latter properties is actually present in a real system.[55] Moreover, the transport of a distribution of charge carriers induces chain deformations (polaronic effect)[56] at a variable extent during the processes of charge transfer and charge recombination (excitons formation)[14t,57] because of the structural flexibility and electronic polarizability of semiconducting organic polymers.[58,59] In these disordered systems charge transport follows mainly the mechanism of variable range hopping[58a,59,60] with polarons having a different extent of spatial delocalization.[61] Different from photogeneration of excitons in an electrically neutral system,[62] excitons formation following the recombination of negative and positive polarons[29b,63] is mainly an intermolecular process in LECs, which gives rise to a uniform front of emission resulting from the electrochemically generated p−n junction.[3,19,40c,40d,64] The emitted intensity and localization of the emissive front in LECs depends on the amount and the relative mobility of the injected charges.[3,19,40c,40d] These are imposed by the electrical current passing through the LEC,[3] the charge transport properties of the various constituents of the LEC,[46,54,65] and the charge-transfer properties through LEC interfaces.[3h,66] In addition to that, the electronic effects associated with the presence of charge-compensating ions, which are present inside the polymer because of doping processes, should also be taken into account in LECs analysis.[3e,40c,65,67] Most of the organic light-emitting materials of interest are in a solid-state configuration or in a condensed phase with mixed electronic-ionic conducting properties.[68] Therefore, ionic-exchange properties with the electrolyte, ionic conductivity, and charge-storage capacitance of the active LEC materials in the doped state strongly affect the organic LECs performance.[3c,3e,19,38a,40c,65,67,69] Charge-compensating ions can influence the electronic and emissive properties of the light-emitting polymer through several ways: (1) the variation of the spacing between polymeric chains (size effect), which affects the interchain electronic hopping;[68b−e] (2) the creation of a local electric field, which controls the dynamics of electronic charge carriers transport in the zone surrounding the ionic sites (electric field effect);[70] (3) the possible formation of mobile charged aggregates which are obtained through the coupling of ionic and electronic charge carriers inside the polymer (coupling effects);[71] (4) possible spin effects on the formation of light-emitting states,[13d,57d,72] which are due to the presence of heavy atoms[73] constituting the dopant (sometimes described as impurity),[74] and participation in the double-layer charging at the electrode/charge-transporting material (CTM) interfaces.[43b,75] A study on the influence of the anion in the supporting electrolyte on the kinetics and stability of a LEC based on the blend of an active luminescent polymer and an ionic polymeric conductor demonstrated that the lower the degree of crystallinity induced by the introduction of the anion in the blend, the lower the response times for the turn on of polymer electrochemiluminescence.[75] This is a consequence of the decrease of ionic conductivity in the blend due to the increase of crystallinity in the polymeric blend and a delay in the formation of the necessary double-layer formation for the onset of the electrochemical processes at the electrode/polymeric blend interface.[75] In some cases, the ions of the supporting electrolyte can participate in the electrochemical processes generating luminescence (case of nonblocking electrode), thus reducing the efficiency of current/light conversion.[75]

Electrochemical and Emissive Processes in LECs. Organic electrochemiluminescent materials must possess an extended conjugated network of π-electrons and accessible unoccupied states in order to make feasible respectively the electrochemical oxidation and reduction of the organic electrochemiluminescent material within a potential range which does not involve any electrochemical decomposition of both constituents (salt and dissolving agent—either liquid or polymeric) of the electrolyte. The electrochemically driven redox processes of organic electrochemiluminescent material are as follows:

$$\mathrm{CM} + \mathrm{e}^- + C^+ \rightleftharpoons (\mathrm{CM}^-)(C^+) \text{ (reduction process at the cathode)} \quad (1)$$

$$\mathrm{CM} + A^- \rightleftharpoons (\mathrm{CM}^+)(A^-) + \mathrm{e}^- \text{ (oxidation process at the anode)} \quad (2)$$

where CM represents a redox-active conjugated moiety participating in the successive generation of the light-emitting exciton (it can be a fully conjugated molecule, or a conjugated portion of an extended molecule like a real polymer), C^+ and A^- are a monovalent cation and anion, respectively, formed after ionic dissociation of the supporting electrolyte in the chosen solvent, and e^- is the negative elementary charge. Since the active organic electrochemiluminescent species considered here are systems which are not dispersed in a liquid solution, but are constituents of a polymeric or solid phase, the occurrence of redox processes implies the uptaking charge-compensating ions from the electrolyte into the reduced (or oxidized) condensed phase and the resulting formation of ionic complexes.[3c,3e,19,38a,40c,65,67,69] If redox processes [1] and [2] occur in semiconducting polymers, then these are also called n- and p-doping or electron- and hole-injection processes, respectively, whereas the radical anion/cation $\mathrm{CM}^{-/+}$ is called a negative/positive polaron if the associated lattice distortion of the conducting polymer is also considered.[76]

In LECs exciton (CM*) formation can be achieved only if at least one of the electrochemically modified species, let us consider CM^-, is able to reach and recombine radiatively with the other electrochemically modified species CM^+ in the present example. As previously outlined, this bears

implications in terms of lifetime and mobility of both electrochemically generated species under concentration and electric field gradients with the possible presence of traps or charge-annihilating impurities.[3a,40b,40d,46] The general mechanism for ECL production from organic redox-active emitters is based on the following steps: (a) Injection of electronic charge carriers with opposite sign in the organic redox-active emitter; (b) transport of the different charge carriers toward a junction (sometimes called (p−n junction),[3b,3j,3m,39a,39b,77] which can be localized inside the light-emitting material (LEM) itself (emission from bulk) or at the borders of the phase which contains the emitter (surface emission); (c) recombination of the different charge carriers in the junction site or zone; (d) formation of electronic excited states as a consequence of recombination; (e) light emission from radiative decay of the electronic excited states.

The light-emitting junction in LECs can be formed through the procedures of double potential step (dps)[40b,40d,46,78] and electrolysis.[3b,3j,3m,39a,39b,77]

In the case of ECL generated with a dps procedure the configuration of the LEC is[40b,46]

[A] metal or ITO/LEM/electrolyte/metal or ITO

In the configuration [A] the working electrode is a thin-film modified electrode,[79] which is obtained by the deposition of the LEM as pure substance[40b,40d,46,80] or molecularly dispersed into a matrix,[18a,81] on transparent ITO or Pt substrates. ECL is obtained upon the sequential stepping of the ITO potential between the values which provoke the oxidation and successively the reduction (or the inverted sequence of electrochemical events), of the deposited LEM. More precisely, ECL occurs during the application of the second step of potential since this represents the only time window of the sequence in which CM^+ and CM^- (eqs 1 and 2) can both coexist in the LEM and, therefore, recombine.[40b−d,46] LEC configuration [A] is characterized by affording both hole and electron injection from the same interface ITO/LEM in a sequential fashion, whereas the other interface LEM/electrolyte is exclusively involved in the processes of ionic exchange necessary for the continuous restoration of electrical neutrality in LEM. If the dps-sequence oxidation−reduction is considered, then the four main steps leading to ECL production in LECs type-[A] are as follows:

(1) Electrochemical formation of oxidized units in CM at the fixed value of potential $V = E_{ox}$:

$$x\mathrm{CM} \rightleftharpoons y(\mathrm{CM}^-) + y\mathrm{e}^- + (x-y)\mathrm{CM} \quad \text{with } x > y \quad (3)$$

In eq 3 x is the total number of redox-active CM units and y is the CM oxidized fraction.

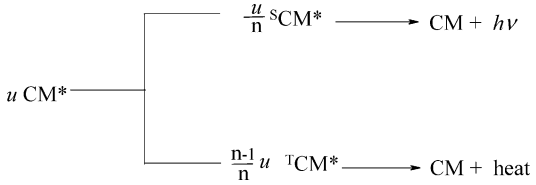
(2) Electrochemical formation of reduced units CM^- from oxidized CM^+ (eq 4a) and neutral CM (eq 4b) at the fixed value of potential E_{red}:

$$y\mathrm{CM}^+ + z\mathrm{e}^- \rightarrow z\mathrm{CM} + (y-z)\mathrm{CM}^+ \quad \text{with } y \geq z \quad (4a)$$

and

$$(x-y+z)\mathrm{CM} + w\mathrm{e}^- \rightleftharpoons w\mathrm{CM}^- + (x-y+z-w)\mathrm{CM} \quad \text{with } x-y+z > w \quad (4b)$$

Chart 1. Electrochemically Generated Organic Excitons in Distinct Spin States and Relative Decay Processes



In eq 4a z is the fraction of oxidized CM^+ units which is neutralized at the second potential step $V = E_{red}$, whereas w in eq 4b is the fraction of netural CM units which is reduced in the second potential step $V = E_{red}$.

(3) Bimolecular recombination of the species CM^+ and CM^- produced respectively in the process of oxidation (eq 3) and reduction (eqs 4a and 4b) with consequent formation of excitons CM* during the second potential step at E_{red}:

$$(y-z)\mathrm{CM}^+ + w\mathrm{CM}^- \rightarrow u\mathrm{CM}^* + a\mathrm{CM} + b\mathrm{CM}^+ + c\mathrm{CM}^- \quad (5)$$

In eq 5 the condition of mass conservation imposes $y - z + w = u + a + b + c$. The factor a indicates the existence of a fraction of recombination events which does not produce excited CM units, whereas b and c indicate the noncompletion of the neutralization process for possible charge-trapping effects (eq 5).[59] The processes described in eqs 4a and 5 have a transient character since CM^+ should be completely consumed ($y - z \rightarrow 0$) at the reduction potential E_{red} of neutral CM (eq 4a) and charge recombiantion (eq 5) unless charge-trapping effect takes place ($y - z$ and $b \neq 0$).

(4) Decay of excitons CM* through radiative and nonradiative pathways[21a] (Chart 1) where $^{S(T)}$CM* is the light-emitting (non-emitting) singlet (triplet) excited state of the organic conjugated material. In Chart 1, n is equal to 4 if statistical formation of the different spin states of excitons is considered.[15a,57d] Analogous equations can be written for the alternative dps sequence reduction−oxidation in which CM^- is formed first, followed by CM^+ formation in the second potential step.[46] For sake of simplicity in eqs 3−5 the exchange of charge-compensating ions C^+ and A^- between LEM and the electrolyte during redox and recombination processes are not described. In LECs having the configuration [A] ECL is a bulk phenomenon since recombination does not occur at an interface but inside the LEM layer itself. Under these circumstances the external quantum efficiency of the device can be somehow negatively affected by self-absorption phenomena if the non-emitting portion of LEM surronding the emitting junction is relatively thick.[27,40c] In LECs with configuration [A] the relative duration of potential steps assumes a particular importance for ECL determination. This is because the duration of a potential step controls the number of injected charge carriers and the extent of their spreading in the LEM layer away from the injecting interface. Both these factors can dramatically affect the kinetics of charge carriers recombination and the possible verification of ECL (eq 5).[46]

The formation of a light-emitting junction via LEM electrolysis has been achieved in LECs having the configuration[3b,3j,3m,39a,39b,50c,69c,77,82]

[B] metal or ITO/LEM-electrolyte blend/metal or ITO

LECs of [B]-type are characterized by the presence of a blend constituted by a mixture of LEM and electrolyte (usually a salt dissolved in gel or a polymer electrolyte), which is sandwiched between metallic electrodes. The blend allows the formation of an interpenetrating LEM/electrolyte interface which favors the ionic transport toward the oxidized and reduced sites of the LEM for the realization of charge compensation processes.[3a,3c,3d,3j,19,35a,44b,83] Moreover, LECs of [B]-type have the advantage of a relatively fast double-layer formation for the onset of the redox processes.[39g,69i,84] In this case, ECL is obtained upon electrolysis of the blend with occurrence of reduction and oxidation of blended LEM at the two distinct metal/blend interfaces. The products of electrolysis CM^+ and CM^- are formed simultaneously at the different metal/blend interfaces and move toward the opposite electrode mainly due to migration, to form the light-emitting p−n junction in the interelectrodic space (Figure 8).[3j,39b,67b]

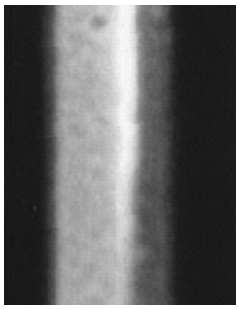


Figure 8. Photograph of the light-emitting junction in a single-layer LEC in which the active layer is a blend of MEH−PPV and the ionic conductor poly(ethylene oxide)/lithium triflate. The thickness of the glowing region is about 15 μm (adapted from ref 42b).

ECL is thus continuously generated as long as electrolysis is running and it is not a by-product in a single step of a sequence like with the dps procedure. Different from type-[A] LECs in which ECL is mainly determined by the choice of the various electrochemical parameters such as applied potential values and step durations within a given LEM system (system under operative control), in type-[B] LECs the phenomenon of ECL is mainly controlled by the nature of the diverse materials in the blend, their composition, and the resulting thickness, which determine in a quasi-univocal way the electrochemical parameters at which ECL is verified (system under configuration control).

In type-[B] LECs, the main steps leading to ECL production are as follows:

(1) Electrochemical formation of oxidized and reduced CM units at the cell potential $\Delta V \geq E_{ox} - E_{red}$ of CM electrolysis:[23a,23b]

$$CM_{blend} + e^- \rightarrow CM^-_{blend} \quad \text{at the cathode} \qquad (6a)$$

$$CM_{blend} \rightarrow CM^+_{blend} + e^- \quad \text{at the anode} \qquad (6b)$$

(2) Displacement of the species CM^+_{blend} and CM^-_{blend} for migration and diffusion from the parent electrode toward recombination zone (junction):

$$CM^-_{blend}\,(\text{cathode}) \rightarrow CM^-_{blend}\,(\text{junction}) \qquad (7a)$$

$$CM^+_{blend}\,(\text{anode}) \rightarrow CM^+_{blend}\,(\text{junction}) \qquad (7b)$$

(3) Bimolecular recombination of the species CM^-_{blend} and CM^+_{blend} produced respectively in the process of reduction (eq 6a) and oxidation (eq 6b) with consequent formation of excitons CM_{blend}* at the junction (see eq 5).

(4) Decay of excitons CM_{blend}* (see Chart 1).

Since in type-[B] LECs the emitting material is blended with the electrolyte, the intermolecular interactions between LEM molecules together with their emissive properties[62a,85] will change depending on the extent of LEM/electrolyte mixing.[3f,44e,86]As a consequence, the value of the wavelength of the radiation emitted by the LEM from the blend can be in principle modulated depending on the LEM concentration in the blend and LEM solubility in the electrolytic component of the blend.[39e,87]

Analysis of LEC Properties and Parameters. In LECs the internal electrochemiluminescence quantum efficiency (η_{int}) can be defined as the ratio of the total number of emitted photons to the number of electrons injected in (removed from) the emitting substance during its reduction (oxidation) process. The evaluation of this parameter is complicated by the problem of photons collection (or viewing) in all directions of emission considering all possible sources of loss of emitted photons.[27] The internal efficiency at a fixed wavelength λ is given by

$$\eta_{int}(\lambda) = N_{el} \cdot \Phi_{exc} \cdot \Phi_{em} \qquad (8)$$

where N_{el} is the number of injected electronic charge carriers (either holes at the anode or electrons at the cathode) at the interface constituted by the electrode/organic emitter (or intermediate hole-/electron-transporting layer),[88] Φ_{exc} is the fraction of injected charges which recombine into neutral excitons, and Φ_{em} is the fraction of excitons which emit light upon decay. The value of n_{el} is determined by the value of the integral of the time-dependent current density j over time t:

$$N_{el} = [\int S \cdot j(t) \cdot dt]/q \qquad (9)$$

In eq 9 S represents the area of the electrode surface and q the elementary charge, which corresponds to the electron charge 1.602×10^{-19} C. In the electroactive material of the LEC the number of injected electronic charge must be compensated through the uptake of an equal amount of charge with opposite in order to preserve electroneutrality.[89] This implies that the amount of supporting electrolyte in a LEC has to be sufficiently high to compensate all the injected charge in the electroactive materials as imposed by the applied potential or current. The fraction of injected charges which recombines to give excitons Φ_{exc} tends to unity if charge-trapping or charge annihilation does not produce considerable effects.[59] Differently, the phenomenon of charge trapping can take place if localized electric fields exist for the presence of quasi-immobile ionic species coming from the electrolyte of the LEC, or for the presence of an uneven distribution of electronic charge caused by structural defects

Table 1. Values of External Quantum Efficiencies for Some LECs

luminescent species	eletrolyte	η_{ext}	refs
MEH−PPV	poly(ethylene oxide)/lithium triflate	>2%	3a, 3b
BDOH−PF	poly(ethylene oxide)/lithium triflate	2.4%	3c, 44a
PPV copolymers	lithium triflate	1.9−2.3%	3t
polyRu(bpy)$_3$	NH4PF6	0.06−0.92%	35e
MEH−PPV	alkylimidazolum salts	0.2−1.4%	38a
MEH−PPV	poly(ethylene oxide)/ammonium salts	0.9−1.5%	39c
BTEM−PPV	lithium triflate	0.35%	87a

(potential wells). This implies that not all injected charges will be able to reach the junction, i.e., the principal zone of emission. The application of sufficiently high fields can bring about the separation of these charged geminate pair with the possible recovery of electronic carriers for active recombination. On the other side, charge annihilation can be caused by impurities with reducing or oxidizing properties, which come into contact with the charge-transporting material.[59] The term related to the fraction of light-emitting excitons Φ_{em} in eq 8, as far as organic emitters are concerned,[90] is mainly limited by the nature of the spin state of the exciton[14u,72,91] due to the restriction imposed by spin-symmetry conservation in the fluorescence process of an organic emitter.[57d,92] In fact, only singlet excitons can decay radiatively to the spin-coupled ground state because atoms with low atomic mass such as the constituents of the organic emitter backbone have scarce probability of promoting mechanisms which lead to the spin-flipping of triplet excitons (intersystem-crossing).[90] Moreover, the rate of phosphorescence from the triplet excited states is nearly zero in such conjugated organic emitting materials.[92a] On the other hand, non-emissive triplet excitons could be converted into active emitting excitons if proper phosphorescent sensitizers are added in the fluorescent organic emitter.[92a,92c,93] Such a procedure has been widely adopted in LEDs whereas only a few examples in LECs have been presented.[94] In the absence of a phosphorescent dopant,[94,95] organic LECs emit light due to a process of fluorescence; i.e., the light-emitting material is in an active state solely when excitation takes place. In fact, ECL in LECs can be classified as a charge-carrier-mediated luminescence[14h] in which recombination processes (electron-transfer event)[15b,96] involve the superposition between the energy levels of ionized states and neutral excited states. The number of ionized states is controlled by the level of injection, whereas formation rate of neutral excited states is mainly determined by the mobilities and lifetimes of the recombining injected charges.[14h,46,65] To a lesser extent, Φ_{em} can also be limited by possible pathways leading to nonradiative decays of the singlet excited states.[97] Another parameter of interest is the external ECL quantum efficiency (η_{ext}), which is defined as the ratio of the detected number of emitted photons by a viewer or a detecting system to the number of electrons injected in (removed from) the emitting substance during its reduction (oxidation) process. The value of η_{ext} is determined by the configuration of the light-emitting cell, the geometry of emission, e.g., lambertian source,[98] and the relative position of the observer (or detector) with respect to the emissive source. At a fixed wavelength of emission λ, η_{ext} is given by the equation[27]

$$\eta_{ext}(\lambda) = \eta_{int}(\lambda)\cdot\Phi_{view} \tag{10}$$

where Φ_{view} refers to the fraction of photons directed toward the viewing direction.

In Table 1 the values of η_{ext} for some LECs are reported.

The emitted intensity I_{em} at a fixed wavelength λ in a LEC is defined as

$$I_{em}(\lambda) = [dE_{em}(\lambda)/dt\ S] \tag{11}$$

in J m^{-2} s^{-1}, with $E_{em}(\lambda)$ representing the total emitted energy at the wavelength of analysis. The latter quantity is obtained by the product of the number of emitted photons with energy hc/λ [$N_{ph}(\lambda)$] to the single-photon energy hc/λ. Alternatively, the emitted intensity from a LEC at a fixed wavelength λ can be expressed in term of photon flux $I'_{em}(\lambda)$ (in m^{-2} s^{-1})

$$I'_{em}(\lambda) = [dN_{ph}(\lambda)/dt\ S] \tag{12a}$$

where $N_{ph}(\lambda)$ represents the total number of emitted photons. The photon flux per unit area can be derived from the densities (or concentrations) of electrons (n_e) and holes (n_h) in the emissive layer from the second-order kinetic model,[14h] assuming excitons to be produced homogeneously throughout the emissive layer as

$$I'_{em}(\lambda) = P_S P_{rad} k_{rec} n_e n_h d \tag{12b}$$

where d is the thickness of the emissive layer, k_{rec} is the rate constant of electron−hole combination, and P_S is the probability of the radiative decay of the singlet excited state. The latter is defined as a ratio of the radiative decay rate constant (k_d) to the total decay rate constant (k_s) of a singlet.

If monochromatic emission is produced by the LEC active material, then $N_{ph}(\lambda)$ can be directly related to the current density of injection j via N_{el} (eq 9) through the relationship

$$N_{ph}(\lambda) = N_{el}{}^2\cdot P_{rad} \tag{13}$$

In eq 13 P_{rad} includes the probability for charge carriers to recombine (P_{rec}) and the probability (P_S) of having a radiative decay from a recombination event producing an excited singlet state since not every recombination leads to the formation of an active emitting excited state, i.e.:

$$P_{rad} = P_{rec}\cdot P_S \tag{14}$$

In eq 12a the derivative $dN_{ph}(\lambda)/dt$ includes both the rate of effective light-emitting charge recombination (k'_{rec}) and k_d, which is related to the time necessary for the excited state to emit a photon.[14h] The constant k'_{rec} can be expressed as the product $k_{rec}\cdot P_S$ where k_{rec} represents the charge recombination rate. Equation 13 retains its validity if charge annihilation processes are negligible in the LEC. In fact, under these conditions the injected charge N_{el} would be equal to the actual number of available electrons N_e and holes N_h

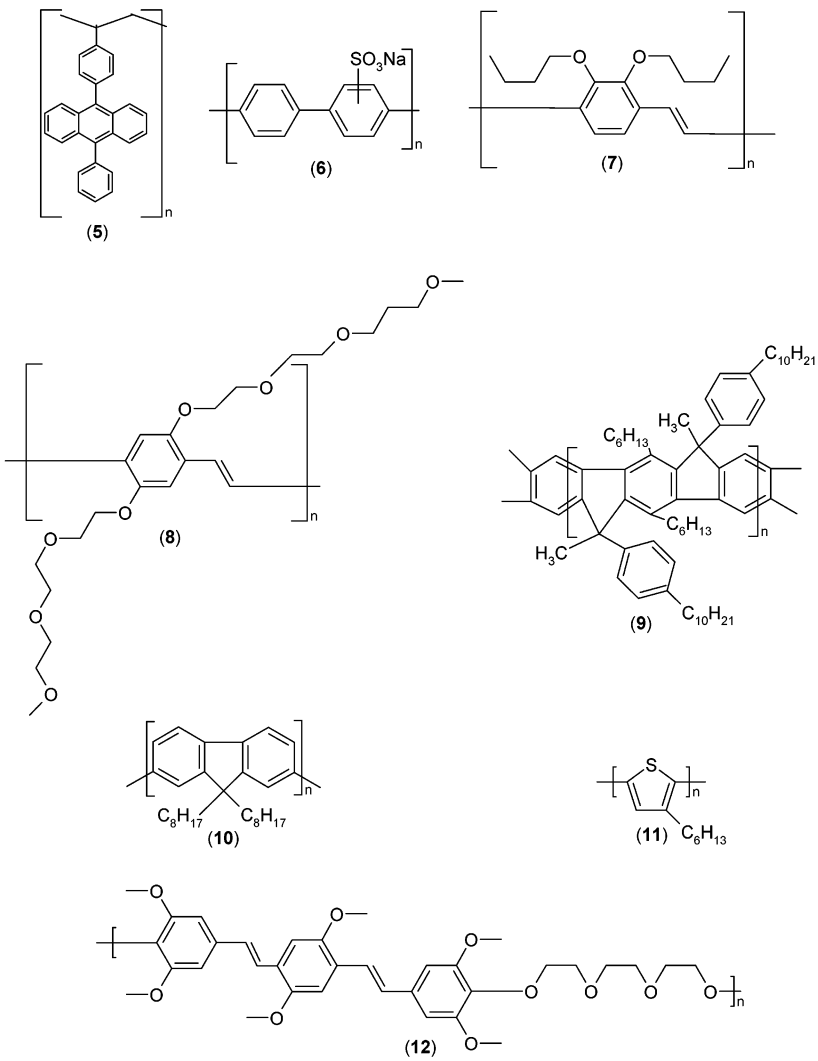


Figure 9. Structures of redox (**5**) and semiconducting (**6**−**12**) polymers known as active organic materials in light-emitting electrochemical cells.

in the emitting material and eq 13 then assumes the form[99]

$$N_{ph}(\lambda) = N_e \cdot N_h \cdot P_{rad} \quad (15)$$

As an electrochemical system, in a LEC the evaluation of the actual injected charge $n_{e/h}$ from the integration of $j(t)$ is affected by the consumption of a capacitive charge which forms the electrical double layer at the electrode/CTM interface before the onset of the actual redox processes, i.e., charge injection.[42,65,89a,100] From the kinetic point of view, this implies the occurrence of a time delay (τ_{dl}) for the double-layer charging at the electrode/CTM interface, which depends on the electronic dynamic polarizability of the molecular CTM contacting the electrode (CTM dielectric properties),[101] the permeability of CTM toward the migration of the ionic charges from LEC electrolyte through CTM layer and the ionic mobility of the charge-compensating ions (CTM ionic conductivity),[3c,3e,19,38a,40c,50c,65,67,102] the orientation of CTM frontier orbitals with respect to the electrode surface (CTM absorption geometry),[103] and the surface density of CTM molecules on electrode surface in organic LECs.[104]

Organic Materials for LECs

As previously outlined, the verification of ECL from molecular materials implies the presence in the molecule of a conjugated network of π-electrons whose electronic states have energy levels which allow charge transfer through electrochemical processes.[21a,46,83d] Besides the conjugated polymer MEH−PPV (**1**)[3a−e,3m,40b,46] (Figure 1), the polymers presented in Figure 9 have also been used as active emissive organic material in solid-state LECs. These include poly(vinyl-9,10-diphenylanthracene) (**5**),[78] which is an example of fixed-site redox conductor having no semiconducting properties, and the semiconducting sulfonated poly(*p*-phenylene) (**6**),[82f] DB−PPV (**7**),[40c] BTEM−PPV (**8**),[39g,40c] ladder-type poly(*p*-phenylene) (m-LPPP) (**9**),[39g] poly(9,9-dioctylfluorene) (**10**) whose ECL has been demonstrated only in solution,[52a] poly(3-hexyl-thiophene) (**11**),[40f] poly[triethyleneoxy-*p*-(diethoxy)phenylenevinylene] (**12**),[105] and others.[3q,106]

In solid-state LECs other emissive molecular materials (which are not strictly organic since they are actually transition metal complexes with organic conjugated ligands) are almost exclusively of the type tris-2,2′-bipyridil-ruthenium-(II) (tris-2,2′-bpy-Ru^{II}). In LECs tris-2,2′-bpy-Ru^{II} complexes can be used as pure compounds (thin film electrodes),[17b,82b] in thin film dispersions with a polymer as solvent, e.g., polystyrene, poly(methyl methacrylate),[69c,82a,82b] and Nafion,[18a,81b] (redox emitter/electrolyte blend), or as pending groups attached to a nonconjugated polymer, e.g.,

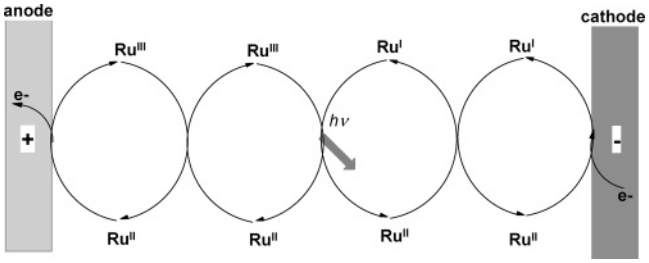


Figure 10. Mechanism of bimolecular electron hopping from right to left in a film of poly[Ru(v-bpy)$_3$](PF$_6$)$_2$ undergoing electrolysis. Light emission is produced upon electron transfer between Ru^{III} and Ru^{II}. Arrows indicate the movement of electrons (counterions migration is not displayed) (adapted from ref 81a).

poly[Ru(4-vinyl-4′-methyl-2,2′-bpy)$_3$(PF$_6$)$_2$].[18b,81a] The processes of tris-2,2′-bpy-Ru^{II} based LECs are described in the case of monolayered LECs in which Ru^{II} complex can be pure,[17b,80a−c,82b] blended,[82a,82b] or attached[81a] in the monolayer sandwiched between the two-cell electrode (Case I) and in the case of multilayered LECs in which Ru^{II} complex can be in the pure state or in a blend constituting the layer in contact with only one electrode and in the presence of a separated electrolytic phase (Case II).[18b,80d]

Case I

In the case of tris-2,2′-bpy-Ru^{II} based monolayered LECs the emitting layer is not involved in mass-exchange processes[17b,69c,80,81a,82a,82b] since charge compensating ions are only displaced for accompanying the electronic carriers motion through the emitting monolayered phase. In this case ECL is produced via electrolysis with the anodic and cathodic processes as reported in eqs 16 and 17.

$$Ru^{II} \rightarrow Ru^{III} + 1e^- \quad \text{at the anode} \qquad (16)$$

$$Ru^{II} + 1e^- \rightarrow Ru^{I} \quad \text{at the cathode} \qquad (17)$$

The recombination mechanism for light emission is

$$Ru^{I} + Ru^{III} \rightarrow {}^*Ru^{II} + Ru^{II} \rightarrow 2Ru^{II} + h\nu \qquad (18)$$

with $h\nu = 1.91$ eV ($\lambda_{em} = 650$ nm) (for sake of simplicity the ligand vbpy is omitted in eqs 16−18).

The mechanism of Ru^{I}/Ru^{III} recombination (eq 18) in emitting Poly[Ru(vbpy)$_3$](PF$_6$)$_2$ film is based on electron-hopping via Ru^{II} sites which oxidize and reduce when at a hopping distance from Ru^{III} and Ru^{I}, respectively (Figure 10).[107] The movement of the counteranions is directed from the cathode toward the anode (not shown in Figure 10).

Case II

Different from Case I, the layer containing emitting Ru^{II} complex is involved in mass-exchange processes due to the demand of electroneutrality in the emitting layer.[18b] In fact, the latter induces exchange of ions from the electrolyte in order to achieve charge compensation inside the Ru^{II} complex containing film. The regenerative ECL produced with such a configuration is obtained with a dps procedure[18b] with alternate formation of Ru^{I} and Ru^{III} which recombine and eventually display ECL according to the mechanism of eq 18.

Conclusions

In the present contribution the electrochemiluminescence produced by organic or molecular emitters in condensed solid or polymeric phases has been reviewed. The technological impact of light-emitting devices which are driven by an electrical current, e.g., light-emitting diodes (LEDs) or electrochemical cells (LECs), has been discussed in the introduction of the present review, stressing the ever-growing role of organic or molecular materials as active materials in these devices. Consequently, a high level of comprehension of electrochemiluminescent phenomena from conjugated organic materials is necessary because of their possible involvement in relevant technologies such as fast-response displays,[32] sensors,[108] chemical imaging,[109] or laser technology.[22] In particular, the advantages of organic LECs over analogous LEDs have been singled out as far as energetic issues were concerned. Successively, the analysis of the phenomena involved in the light-emission processes generated in LECs has been carried out describing the mechanisms at the basis of the electrochemical and emissive processes in LECs. Particular emphasis has been given to the issue of charge transport (both electronic and ionic) since this aspect has a paramount role in the kinetics of light emission in LECs. After the analysis of the chemical-physical mechanisms operating in LECs, the definition and the usefulness of the various parameters defined for the evaluation of LECs performances have been discussed. Finally, a review of the active organic or molecular materials used in LECs is presented together with the description of the various LECs configurations and their main characteristics.

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