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Faculty of Mathematics and Sciences
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M7 ELECTROLUMINESCENCE OF POLYMERS

I. Introduction

The recombination of holes and electrons in a luminescent material can produce light. This emitted light is referred to as electroluminescence (EL) and was discovered in organic single crystals by Pope, Kallmann, and Magnante (1963). EL from conjugated polymers was first reported by Burroughes et al. (1990). The polymer used was poly (p-phenylenevinylene) (PPV). PPV has excellent mechanical properties, good flexibility and is stable to 400°C.

EL-devices have potential applications in a wide field ranging from multi-color displays to optical information processing. Polymers have the advantage over inorganic and monomolecular materials in the ease with which thin, structurally robust films can be made and large areas covered by spin-coating a polymer from solution. Even flexible displays can be produced because of the good mechanical properties of polymers.

I.1. Light-Emitting Diodes

In the following, only so-called light-emitting diodes (LEDs) are discussed. A simple LED device geometry is shown in Figure I.1. It consists of one emission layer sandwiched between a hole and an electron injecting contact, denoted anode and cathode, respectively. In these devices, carriers of opposite sign are injected separately at opposing contacts when a sufficiently high voltage is applied. These carriers are mobile under the influence of the electric field.

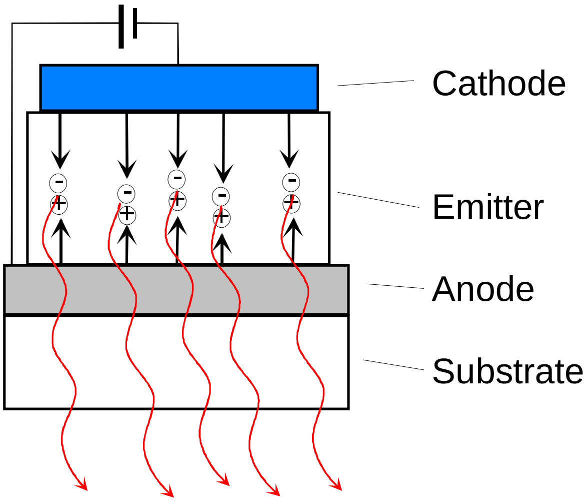


Fig. I.1: Schematic drawing of a single-layer electroluminescent diode. An applied electric field leads to injection of holes and electrons into the light-emitting film from the two electrode contacts. Formation of an electron-hole pair within the material may then result in the emission of a photon.

Figure I.2 gives a schematic description of the EL from anthracene provided with opposing Na and Au injection contacts. Some of these carriers may recombine within the emissive layer yielding excited electron-hole pairs, termed excitons. In a molecular picture such an exciton represents an excited electronic state, e.g. S_1, of the anthracene molecule, which can decay either radiatively (under emission of a photon) or non-radiatively (under production of heat) to the groundstate S_0.

Based on the spin-statistics, this produces singlet and triplet excitons in the ratio 1:3 (Figure I.3). The singlet excitons (S*) decay promptly, yielding what is referred to as prompt EL, whereas the triplet excitons either decay directly (electrophosphorescence) or they fuse to form singlet excitons, producing delayed EL, (S_d^*).

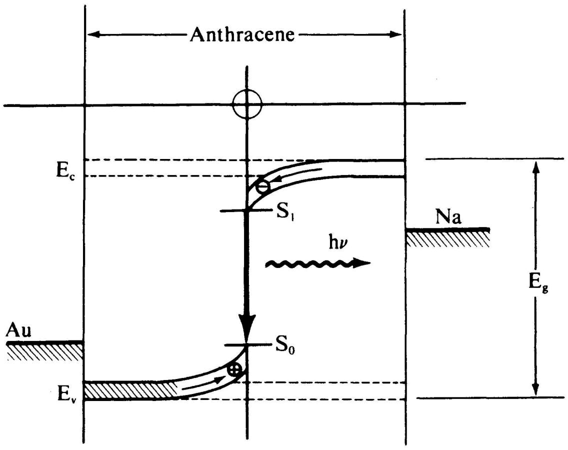


Fig. I.2: Schematic view (not to scale energetically) of electron-hole recombination in anthracene after injection from Na and Au, respectively. Violet light is generated with a quantum yield of about 20 per cent. The dotted lines represent the energy separation of the valence and conduction level carriers in the absence of any interactions between the carriers. The solid lines indicate the energy separation of the injected valence and conduction level carriers in the course of recombination.

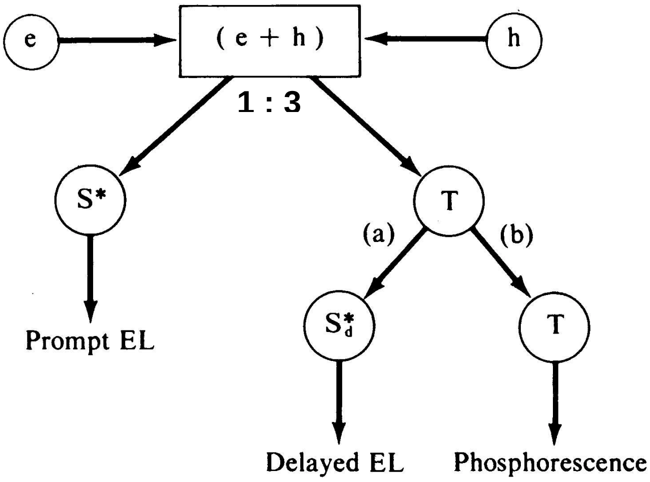


Fig. I.3: Simplified decay scheme of the excitation produced by recombination of an electron-hole pair. S^*_d, S, and T denote primary singlet, delayed singlet, and triplet excitons, respectively. Process (a) represents the bimolecular annihilation (fusion) of two triplet (T) excitations. Process (b) represents the direct radiative decay of the triplet state.

The simplest polymer-based LED (Figure I.4) consists of a single layer of semiconducting fluorescent polymer, e.g., PPV, sandwiched between two well known electrodes, a semitransparent, high work function anode (ITO, Au, etc.) and an opaque, low work function cathode (Ca, Mg, Al, etc.). The thickness of the organic layer is typically in the order of 100 nm and, for experimental convenience, the active device area is in the order of a few mm^2. More elaborated multilayer structures (Figure I.5) include additional charge-transporting layer. The role of e.g. the hole-transporting layer is to facilitate hole transport from the anode to the emission layer and to prevent electrons to leave the emission layer and reach the anode without recombining with a hole.

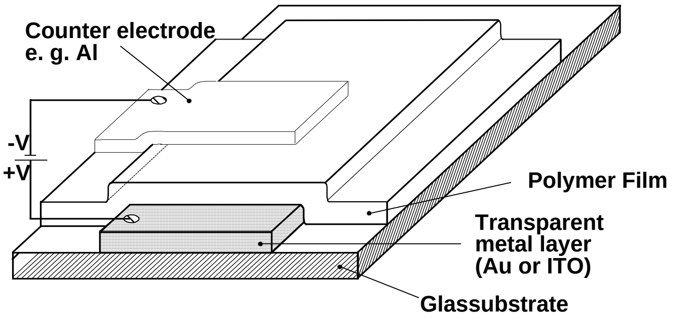


Fig. I.4: Layout of a simple polymer-based light-emitting diode.

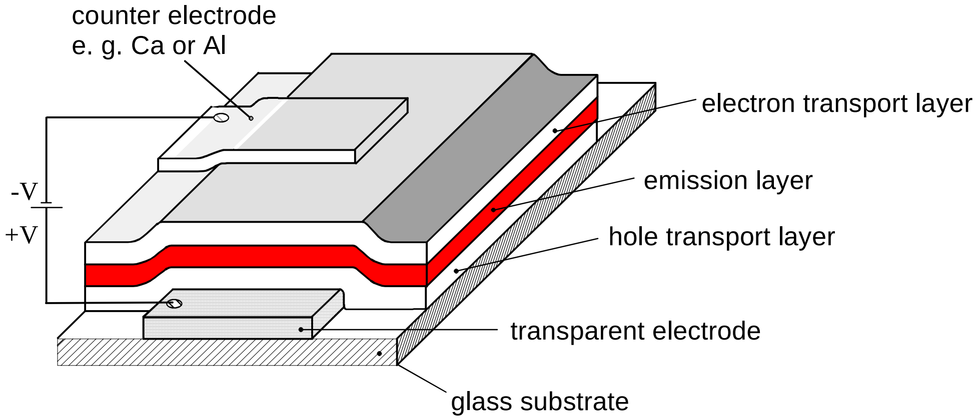


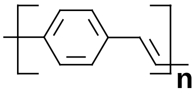
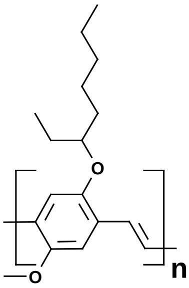
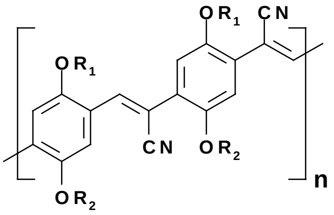
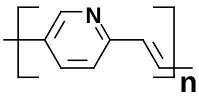
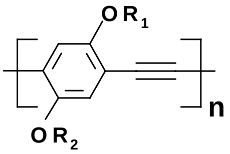
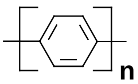
Fig. I.5: Layout of a multilayer LED comprising hole and electron-transporting layers.

I.2. Polymers for Light-Emitting Diodes

I.2.1. Overview

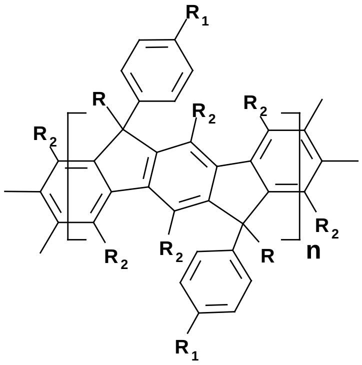
In general, the polymer forming the emission layer must be able to produce light by the recombination of singlet excitons. In addition, it must be able to transport charges (holes and electrons). The following Table 1 shows a selection of polymers which has been mostly studied with respect to EL. All polymers have in common that they possess a π-conjugated electron system as the active chromophore and that this conjugated systems forms the polymer backbone. Other polymers have been used which are build from an inactive (saturated backbone) bearing chromophore-containing side chains. In the following, we concentrate on poly [2-methoxy, 5-(2´-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV), a derivative of poly(p-phenylene vinylene) (PPV).

Table 1: Polymers, which have been extensively studied for EL

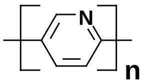
PPV poly(p-phenylene vinylene)	
MEH-PPV poly[2-methoxy-5-(2´-ethyl-hexoxy)-1,4- phenylene vinylene	
CN-PPV (R_1=R_2=C_6H_{13}) poly[2,5-bis (hexyloxy)-1,4-phenylene-1-cyanovinylene)]	
PPyV poly(p-pyridyl vinylene)	
DHO-PPE (R_1=R_2=hexyl) poly[1,4-(2,5 dihexoxy)-phenylene ethynylene)]	
PPP poly(para-phenylene)	

LPPP

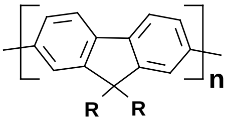
“ladder-type poly(para-phenylene)”



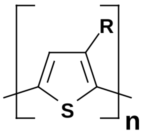
PPy
poly(p-pyridine)



PDAF
poly(9,9-dialkylfluorene)



P3AT
poly(3-alkylthiophene)



I.2.2. Optical properties

The optical absorption and electroluminescence emission spectra of MEH-PPV are shown in Figure I.6. The absorption and emission spectra are typical of PPV-based polymers. The maximum absorption coefficient is about $2.5\text{x}10^5$ cm^{-1}. The absorption has a broad peak, which is roughly 0.5 eV wide with vibronic features evident at about 2.2 eV and 2.4 eV. The energy gap of MEH-PPV is about 2.4 eV. The electroluminescence emission spectrum peaks at about 2 eV and also contains several vibronic peaks. The diode electroluminescence spectrum is broad, roughly 50nm wide. The width of the absorption and emission spectra is partially due to the disorder in the film. Ladder polymers that contain linking groups that preserve the structure of the polymer chain have considerably sharper spectral features. The photoluminescence spectrum (not shown) is identical to the electroluminescence spectrum indicating that the excitations produced optically and electrically are identical. The red shift in energy between the optical absorption and emission peaks of about 0.2 eV is typical of electroluminescent polymers.

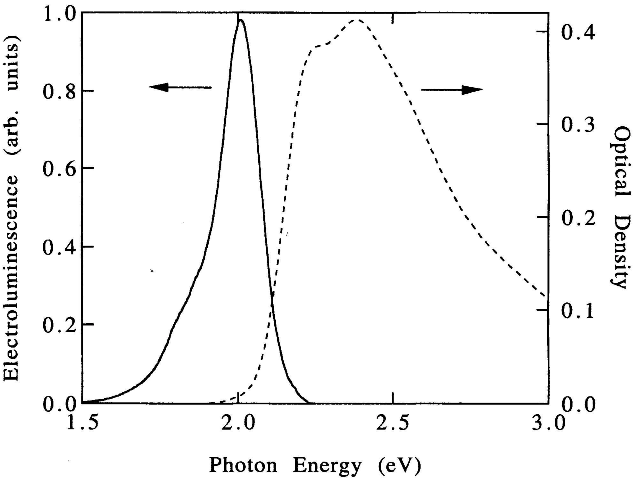


Fig. I.6: Electroluminescence and optical absorption spectrum of the soluble polymer MEH-PPV.

I.2.3. Color

The emission color of a polymers depends strongly on the chemical structure of the polymer. PPP shows emission with a peak wavelength of approx. 420 nm, that is far in the blue. The emission maximum shifts to longer wavelength when the phenyl rings in PPP become rigidly connected as in PF and LPPP. Unsubstituted PPV emits green light, but the emission color can be tuned to the red by appropriate substitution. Finally, PT is a red emitter. It should be noted that the PL spectra in solution and in the solid state might be different due to intramolecular effects in the solid state. Also, the EL spectrum might differ from the solid state PL spectrum due to the difference in excitation mechanism (PL is generated by light absorption, EL by the recombination of charge carriers).

I.3. Efficiency Considerations

The efficiency of organic LED devices is described by several parameters. The internal quantum efficiency $\eta_{int}(EL)$ is defined as the number of photons generated in the material per injected charge carrier. If emission occurs through the radiative decay of singlet excitons, (no phoshorescence) the upper limit of η_{int} is given by

$$\eta_{int}(EL) = \frac{1}{4}\,\eta(PL) \tag{1}$$

with $\eta(PL)$ the solid state photoluminescence quantum efficiency. The factor 1:4 stems from the fact the recombination of “uncorrelated”charge carriers yields singlet and triplet excitons in a ratio 1:3. Since only singlet excitons decay radiatively in most polymers at room temperature, the probability that a carrier recombination yields an emissive exciton is 1:4. In general, not all but only a fraction $\phi_r < 1$ of all injected carriers will recombine and $\eta_{int}(EL)$ then is given by

$$\eta_{int}(EL) = \frac{1}{4}\, \eta(PL)\, \phi_r \tag{2}$$

The external quantum efficiency $\eta_{ex}(EL) < \eta_{int}(EL)$ is defined as the number of „detectable“ photons per injected charge carrier. For an isotropic material, where the transition dipoles are randomly oriented,

$$\eta_{ext}(EL) = \frac{\eta_{int}(EL)}{2n^2} \tag{3}$$

(n is the refractive index of the organic layer). For ideal recombination conditions $\phi_r = 1$, $\eta(PL) = 1$ and a refractive index n of 1.7, the maximum external efficiency is approx. 5 %

Relevant for a device application is the external power efficiency $\eta_P(EL)$, defined as the emitted light power divided by the electrical driving power. Using the definition of the external quantum efficiency, $\eta_P(EL)$ can be rewritten as

$$\eta_p(EL) = \frac{\omega}{eU}\, \eta_{ext}(EL) \tag{4}$$

where ω is the energy of the emitted photons and e is the electric charge of an electron. Note, that this expression is absolutely correct only for monochromatic light emission A high power efficiency thus requires a high external quantum efficiency $\eta_{ext}(EL)$ and a low operating voltage U.

For an external efficiency of 5%, an operating voltage of 3 V and an emission wavelength of 540 nm ($\omega = 2.3$ eV), $\eta_P(EL) \cong 4$ %

II. Theory of Electroluminescence

Electroluminescence in organic layers involves a series of steps:

1) Injection of the charge carrier from a metal contact into the organic layer

2) Transport of the charge carrier within the film and recombination of hole and electron followed by the formation of excitons

3) Migration and radiative decay of the exciton

4) Emission of the generated photon to the outside

The efficiency of these processes is closely related to the device geometry and to particular properties of the applied polymers such as the positions of energy levels of the charge transport materials or the solid state photoluminescence efficiency of the emitting polymer.

II.1. Charge Injection

One of the fundamental processes occurring in polymer LEDs is charge injection form the metal contacts into the electroluminescent polymer film. This charge injection can be qualitatively understood by considering the electronic energy structure of the thin polymer film. The electronic energy structure of a PPV film is shown in Figure II.1 along with the work function of various metals used as contacts in polymer LEDs. The ionization potential (E_v) of PPV, i.e. the energy required to remove an electron from the highest occupied state (HOMO) to vacuum, is roughly 5.2 eV. The electron affinity (E_c), i.e. the energy gained when adding an electron to the lowest energy unoccupied state (LUMO) from vacuum, is roughly 2.5 eV. The energy gap, $E_v - E_c$, is about 2.7 eV. To inject electrons the contact must be able to donate electrons into the lowest unoccupied state 2.5 eV below vacuum. Similarly, to inject holes (remove electrons) the contact must be able to accept electron from an energy 5.2 eV below vacuum.

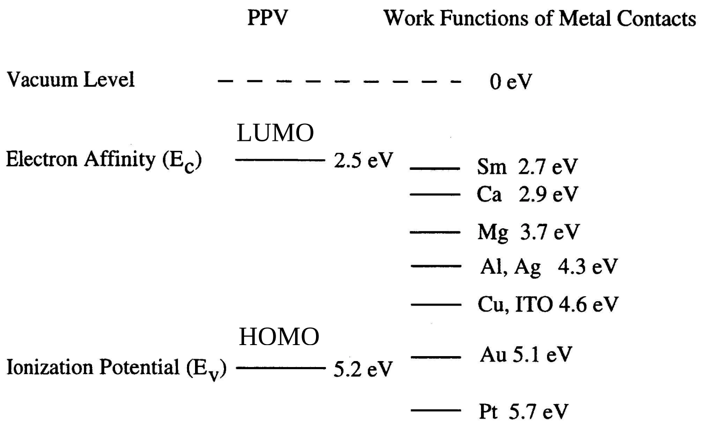


Fig. II.1: Electron energy level diagram of PPV and work functions of selected contact metals used in polymer LEDs.

Electron injection is thus limited by the barrier $\Delta\phi_e$ between the Fermi level of the cathode and the position of the LUMO (given by the adiabatic electron affinity). The rate of hole injection is similarly determined by the barrier $\Delta\phi_h$ between the work function of the anode material and the HOMO (given by the adiabatic ionization energy) of the polymer.

The injection of charge carriers from an electrode into an organic layer has been extensively treated by Parker (1992). At high fields, the current densities can be described by the tunneling of the charge carriers through a rectangular barrier (Figure II.2). The Fowler-Nordheimer theory gives:

$$j \propto F^2 \exp\left(-\frac{8\pi\sqrt{2m^*}\,\Delta\phi^{3/2}}{3ehF}\right) \qquad (5)$$

Here, F is the internal electric field, m^* the effective mass of the electron in the organic semiconductor (set equal to the electron mass in free space) and h the Planck constant. The plot $\ln(j/F^2)$ versus $1/F$ yields the barrier high $\Delta\phi$. The Fowler-Nordheimer theory predicts a strong dependence of $j_{e/h}$ on $\Delta\phi_{e/h}$ and the applied electric field. Since many π-conjugated polymer have ionization energies of about 5 eV, high work function materials such as gold, copper and indium-tin-oxide (ITO) are suitable for hole injection. LUMO positions are typically located between 3 eV and 1.5 eV. Effective electron injection thus requires low work function metals such as calcium. However, these metals are very unstable in air and require device encapsulation. For a balanced charge injection similar barriers $\Delta\phi_e \cong \Delta\phi_h$ are needed. In most polymeric systems, balanced charge injection is difficult to realize in single layer devices.

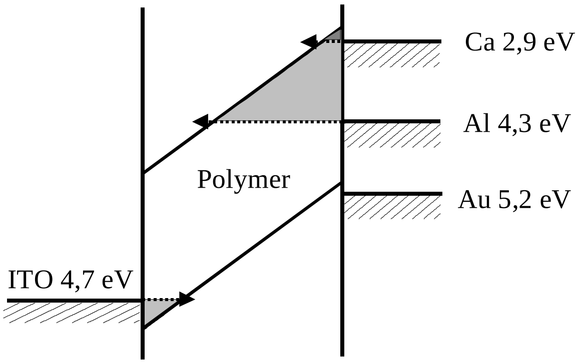


Fig. II.2: Band diagram for electron and hole injection into a polymer layer

If the work function of the two contacts is different, the current will not only depend on the absolute field but also on its direction. Higher currents will flow if the contact with the higher work function is biased as the anode and the contact with the smaller work function as the cathode. This situation is denoted forward bias. Inverting the bias (reverse bias) will lead to smaller currents, why this behavior is called diode-like current-voltage characteristics (Figure II.3).

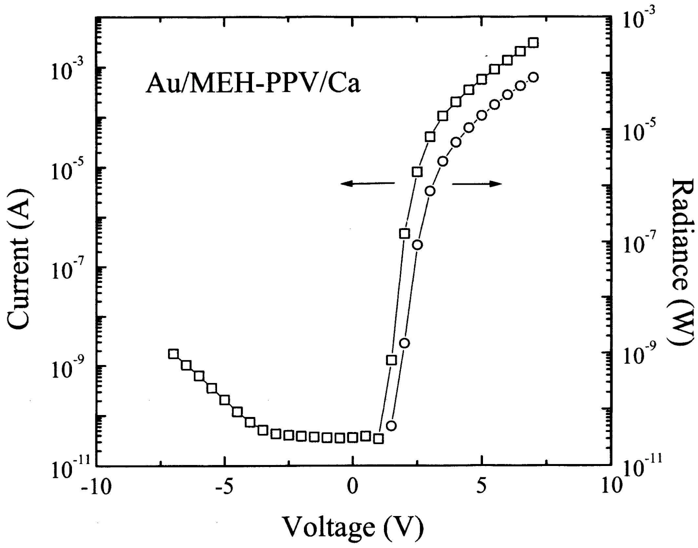


Fig. II.3: Typical current-voltage and radiance-voltage characteristics of an MEH-PPV-based OLED with an Au anode and a Ca cathode.

II.2. Charge Carrier Motion and Recombination

The motion of charge carriers is generally described by the carrier mobility μ, which is defined by the ratio of the drift velocity v and the electric field F:

$$\mu = \frac{v}{F} \tag{6}$$

In typical conjugated polymers the mobility for holes is in the range 10^{-7} - 10^{-3} cm^2/Vs. Because of oxygen contamination the mobility of electrons in these polymers is generally lower.

The recombination of an electron and a hole under the condition of low mobility is described by the Langevin recombination mechanism, which involves the drift of one of the charges in the electric field of the other partner. Thus, the decay rate is much smaller than the radiative life time of the exciton and controlled by the mobility and densities of the charge carriers. Efficient diodes with the recombination of all injected charges is only possible at high current levels under certain conditions.

II.3. Migration and Radiative Decay of the Excitons

A critical parameter in determining the operating efficiency of polymer LEDs is the luminescence quantum efficiency $\eta(PL)$ of singlet excitons in the polymer i.e. the probability that a singlet excitons will decay radiatively. This probability is limited by the intrinsic (intramolecular) quantum efficiency for radiative decay on an isolated molecule (as determined by the PL efficiency in dilute solution). However, in the solid state, several mechanisms can further reduce the quantum efficiency: a) electronic coupling to neighboring molecules might alter the electronic states and thus the efficiency for radiative exciton decay; (b) during its lifetime (typically 100 ps - 1 ns) the exciton in polymers can diffuse to nonradiative sites (so-called quenching sites) or they might be deactivated at the metal electrodes via energy transfer or dissociation. Therefore, the photoluminescence quantum efficiency $\eta(PL)$ in the solid state is generally smaller than in dilute solution. For “good” polymers, values range between 40 % and 60 %. For MEH-PPV, efficiencies of approx. 15 % have been reported.

II.4. Emission of the Generated Photon to the Outside

Not every photon generated inside the emission layer will escape the device and become visible to an external observer. Photons might be absorbed either by the emissive material itself (reabsorption), by additional charge transport layers or by the electrodes. Further, the refractive index n_p of the emissive polymer (typically 1.7-2.0) is larger than that of the supporting glass substrate ($n_s \approx 1.5$). Thus, photons generated in the polymer layer, propagating at an oblique angle with respect to the surface normal, are totally reflected at the polymer-glass interface and waveguided in the device. To a first approximation, only a fraction $1/(2n_p^2)$ of the internally generated photons are emitted to the outside.

III. Emitted Power and Brightness

III.1. Comparison of radiometric (physical) and photometric (physiological) quantities

Photometric quantities represent the visible part of the optical radiation field. Photometry provides physiological insight to the optical radiation field detected by the human eye. On the other hand, radiometry refers to the energy content of the optical radiation field.

radiometric	***photometric***
Consider a light source *S* (Figure III.1) with an area *A*, which emits an electromagnetic field into the space above the source.	
The energy emitted within this radiation field is the **radiant energy Q_E** which is measured in joules (1 J = 1 Ws).	The **luminous energy Q_v** is the energy of the visible radiation field. It is measured in lumens·sec (lm·s).
The radiant energy emitted per time $\Phi_E = \frac{dQ_E}{dt}$ (7a) is introduced as the **radiant power** or **radiant flux Φ_E,** which is measured in watts (W). The radiant flux represents an instantaneous radiometric quantity.	The **luminous flux Φ_v** is defined as $\Phi_v = \frac{dQ_v}{dt}$ (7b) and is measured in lumens (lm).
The radiant flux per unit solid angle emitted by a source along a given direction $I_E = \frac{d\Phi_E}{d\Omega}$ (8a) is introduced as the **radiant intensity I_E**; it is measured in watts per steradian (W·sr^{-1}).	The **luminous intensity I_V** is defined as the luminous flux through the solid angle dΩ: $I_v = \frac{d\Phi_v}{d\Omega}$ (8b) It is measured in lm·sr^{-1}, which is also referred to as candela (cd) (basic unit of SI).
With regard to the geometry of Figure III.1, the solid angle dΩ subtended by the surface element $\overrightarrow{ds} \parallel r$ is given by $d\Omega = \frac{ds}{r^2}$ (9)	
Finally, the emitted radiant intensity per unit emitting area dA (Figure III.2) is introduced as the **radiance L_E** of an extended source in that direction. In this definition, only the apparent emitting area that is the source area projected on a plane perpendicular to the observation direction $\hat{r}$ is taken into account: $L_E = \frac{dI_E}{d\vec{A}\cdot\hat{r}} = \frac{1}{\cos\theta}\frac{dI_E}{dA}$ (10a) It is evident that L_E is measured in W·m^{-2}·sr^{-1}.	Finally, the brightness of a source is expressed by the **luminance L_V**: $L_v = \frac{dI_v}{d\vec{A}\cdot\hat{r}} = \frac{1}{\cos\theta}\frac{dI_v}{dA}$ (10b) L_v is measured in lm·m^{-2}·sr^{-1} (cd·m^{-2}). definition : 1 cd is the luminous intensity of a black radiator with the temperature T = 1770 °C (melting temperature of platinum) and an opening of 1/60 cm^2.

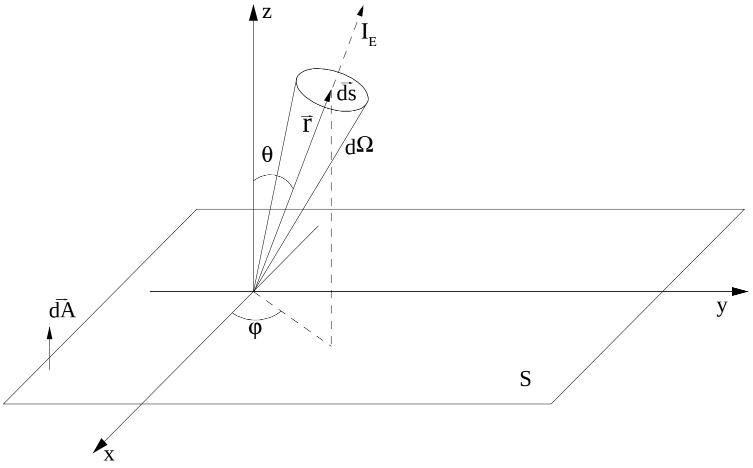


Fig. III.1 : Sketch to define the radiometric quantities of light emitted from the light source S

III.2 Lambert‘s radiator

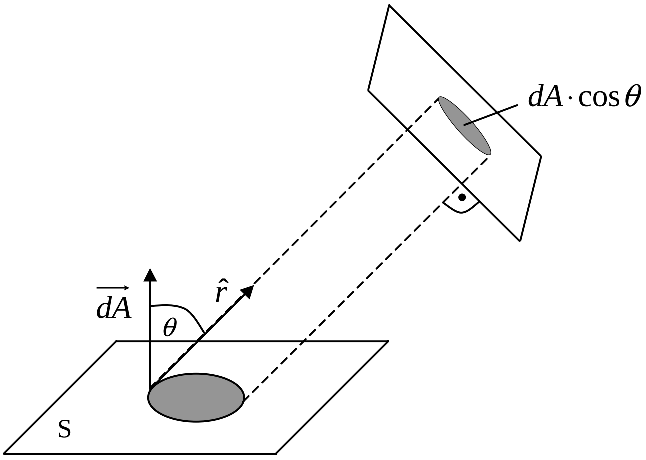


Fig. III.2 : Projection of an emitting surface element of an extended source

Consider a Lambert’s radiating surface where each point even radiates into the room 2π, an angle dependence of the visible surface (Fig. III.2) is observed with an effective surface of :

$$dA_{eff} = \overrightarrow{dA} \cdot \hat{r} = dA \cdot \cos\theta \,. \tag{11}$$

The luminous intensity in θ - direction ($I_{V,\theta}$) follows with (11)

$$I_{V,\theta} = I_V \cos\theta \tag{12}$$

with I_V = luminous intensity normal to the surface

θ = angle between $\overrightarrow{dA}$ and direction of observation

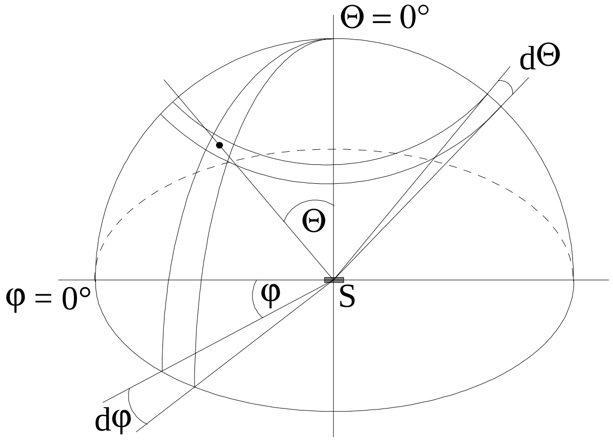


Fig. III.3 : Illustration of half-room above the source

For a Lambert's radiator the connection between luminous flux and luminance follows from the integration over the half-room above the radiating source (Fig. III.3)

$$
\begin{aligned}
L_V &= \frac{dI_V}{\cos\theta \cdot dA} = \frac{d^2\Phi_V}{\cos\theta \cdot dA \cdot d\Omega} \\
d^2\Phi_V &= L_V \cdot \cos\theta \cdot dA \cdot d\Omega
\end{aligned}
$$

$$
\begin{aligned}
\Phi_V &= \int d^2\Phi_V = \int L_V \cdot \cos\theta \cdot dA \cdot d\Omega \\
&= L_V \cdot A \int_0^{2\pi} \cos\theta \cdot d\Omega \\
&= L_V \cdot A \int_0^{2\pi}\int_0^{\pi/2} \cos\theta \sin\theta \, d\theta d\varphi \\
&= \tfrac{1}{2} L_V \cdot A \int_0^{2\pi}\int_0^{\pi/2} \sin 2\theta \, d\theta d\varphi \\
&= \tfrac{1}{2} L_V \cdot A \int_0^{2\pi} \tfrac{1}{2}\cos 2\theta \Big|_{2\pi}^{0} d\varphi = \tfrac{1}{2} L_V \cdot A \int_0^{2\pi} 1 \, d\varphi \\
&= L_V \cdot A \cdot \pi \ sr \qquad (13)
\end{aligned}
$$

Thus, a Lambert's radiator with an emitting area of 1 m^2 and a luminance of 100 cd/m^2 corresponds to a luminous flux of 314 lm.

$$
\begin{aligned}
\Phi_V &= 100\, cd/m^2 \cdot 1 m^2 \cdot \pi \ sr \\
&= 314\, cd\ sr \\
&= 314\, lm
\end{aligned}
$$

The most important parameter for characterizing a light source is the luminance. For example, a computer screen should have a luminance of 100 cd/m^2.

A second quantity connected to this is the luminous efficiency

$$\eta_{el} = \frac{\Phi_V}{P_{el}} \quad [\mathrm{lm/W}] \tag{14}$$

which is the luminous flux related to the electrical input power.

III.3. Connection between Radiometric and Photometric Quantities

It is useful to establish a link between the radiant flux and the luminous flux, thus relating physical units to physiological ones. Since the human eye, our own light detector, is characterized by non-uniform sensitivity to the various spectral components of light, an experimental function, the spectral eye sensitivity V_λ (Figure III.3), is used to represent the physiological effect of light throughout the visible part of the spectrum. At maximum of the sensitivity curve (λ_m = 555 nm) a luminous flux of 680 lm represents a radiation flux of 1 W. The wavelength-dependent factor V_λ is obviously required to convert watts to lumens throughout the spectrum.

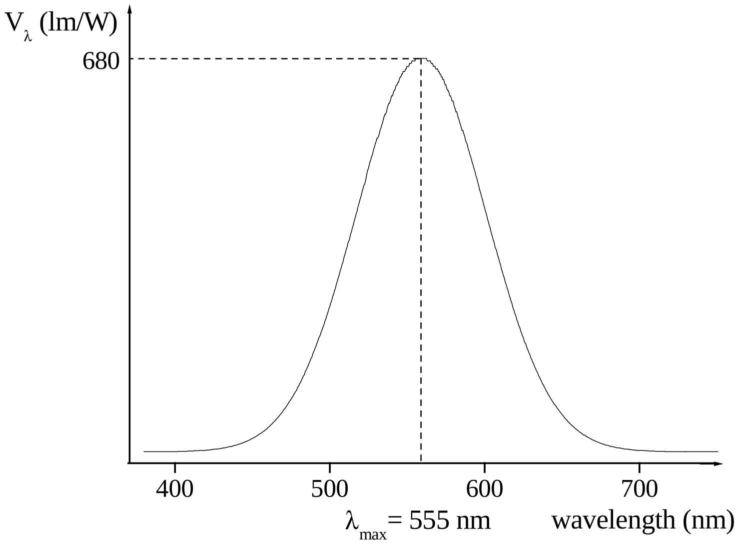


Fig. III.3: Eye-sensitivity V_λ with the maximum sensitivity at λ = 555 nm as a function of wavelength.

The values s_λ of corrected measured emission spectra correspond to the number of registered photons. The photon number, received in a room angle Ω determined by the equipment (Fig. III.4) is related to the spectral band width $\Delta\lambda$ = 10 nm at the wavelength λ in a defined time interval Δt =1s. Thus, the spectral radiant intensity follows to

$$i_{E,\lambda} = \frac{dI_E}{d\lambda}|_\lambda = f_{cal} \cdot \frac{s_\lambda}{10nm \cdot \Omega} \cdot \frac{hc}{\lambda} \ , \qquad (15)$$

whereas the total spectral radiant flux of a Lambert’s radiator is

$$\begin{aligned} \varphi_{E,\lambda} &= \frac{d\Phi_E}{d\lambda}|_\lambda \\ &= i_{E,\lambda} \cdot d\Omega \qquad . \qquad (16) \\ &= f_{cal} \cdot \frac{s_\lambda}{10nm \cdot \Omega} \cdot \frac{hc}{\lambda} \cdot \pi sr \end{aligned}$$

In consideration of the eye-sensitivity V_λ the spectral luminous flux $\varphi_{V,\lambda}$ (lm /nm) behaves

$$\varphi_{V,\lambda} = V_\lambda \cdot \varphi_{E,\lambda} . \qquad (17)$$

Integration of the spectrum with respect to results in the overall emitted luminous flux Φ_V (lm). Moreover the spectral radiant flux delivers the overall emitted radiant flux Φ_E (W).

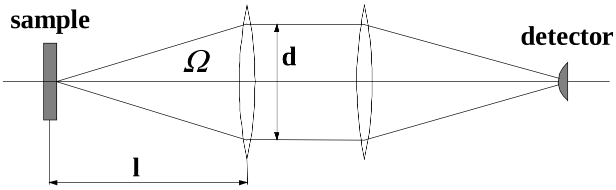


Fig. III.4 : Illustration of the room angle Ω for the measurement configuration

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IV. Experiments

1. Instrumentation

1.1. Determine the correction function for the excitation spectra

1.2. Determine the correction function for the emission spectra

2. Photoluminescence Spectroscopy

2.1. Measure the photoluminescence emission spectra for a thin film of MEH-PPV at an excitation wavelength of 465 nm. Perform the measurement for front face illumination and with the inline geometry

3. Electroluminescence

3.1. Measure the voltage U as a function of the current I through the LED ($U = f(I)$) and the spectral radiant intensity of electroluminescence $i_{E,\lambda}$ respectively the related uncorrected signal $s_{\lambda,uncorr}$ as a function of the current ($s_{\lambda,uncorr} = f\ (I)$). Analyze the $U(I)$ data according to the Fowler-Nordheimer equation with respect to the barrier height $\Delta\phi$. The thickness oft the polymer layer is approx. 100 nm.

3.2. Measure $s_{\lambda,uncorr}$ as a function of the viewing angle. Analyze the data according to Lambert's law. Is the law fulfilled?

3.3. Measure the electroluminescence spectrum $s_{\lambda,uncorr}(\lambda)$ at a current of approx. 2 mA. Compare the spectrum to the photoluminescence emission spectrum. Are they different? What do you conclude concerning the origin of electroluminescence?

3.4. Make an absolute calibration of the detection unit using a calibrated diode with a given radiant power Φ_E. What is the radiant power Φ_E and the radiance L_E of the polymer LED at approx. 2 mA? Using the eye sensitivity V_λ , determine the luminance L_v and the luminous efficiency of the polymer LED.

V. Remarks to the Instrumentation

V.1. Correction of Spectra

Photoluminescence, excitation and electroluminescence spectra are measured with a modular fluorescence spectrometer.

Because of the characteristics of optical components the observed signal in excitation and emission measurement is distorted for several reasons:

- The light intensity from the excitation source is a function of wavelength. The intensity of the exciting light can be monitored via a beam splitter, and corrected by division.

- The efficiency and the polarizing effect of the monochromators are a functions of wavelength.

- The optical density of the sample may exceed the linear range, which is about 0.1 absorbance units, depending upon sample geometry and the slit width of monochromators.

- The emission spectrum is further distorted by the wavelength dependent efficiency of the photodetector.

For discussion of the individual components of a spectrofluorometer (see J.R. Lakowicz, “Principle of Fluorescence Spectroscopy”, Plenum Press (1983), ISBN 0-306-41285-3).

The development of methods to correct excitation and emission spectra (photo- and electroluminescence) for wavelength dependent effects has been the subject of numerous investigations. Overall, none of these methods are completely satisfactory. Prior to correcting spectra the researcher should determine if such corrections are necessary. Frequently, one only needs to compare spectra with other spectra collected on the same instrument. Corrected spectra are needed for calculations of quantum yields and overlap integrals.

Corrected excitation spectra

The wavelength dependent intensity of the exciting light can be converted to a signal proportional to the number of incident photons by the use of a quantum counter. The concentrated solution of Rhodamin B in ethylene glycol absorbs all incident light and provides a signal of constant wavelength, which is proportional to the photon flux of the exciting light L(8) – the emission spectrum is independent of excitation wavelength.

If there is not a reference detection channel the emission intensity of Rhodamin is recorded by use of a triangular cuvette instead of the sample, like an excitation spectrum. All recorded excitation spectra have to be divided by the “Rhodamin excitation spectrum” to obtain the corrected excitation spectra.

Corrected emission spectra

The correction of emission spectra requires knowledge of the wavelength dependent efficiency of the detection system, all components the emission light has to pass and the detector. The wavelength dependent correction factor is generally obtained by the measurement of light of a known spectral distribution. The sensitivity of the detection system S(8) is calculated as the ratio of the measured signal I(8) and the known spectral intensity distribution of detected light. This standard spectrum can be

- the emission spectrum of a standard substance,

- the wavelength dependent output from a calibrated light source, e.g. a tungsten filament lamp of known color temperature or

-the spectral distribution of the exciting light produced by a Xe-lamp and a wavelength independent scatterer, MgO.

In the last case the scatterer is placed in the sample compartment. Whereas light of a selected wavelength passes the excitation monochromator the scattered light is measured at the same wavelength by a synchronous scan. Dividing the intensity distribution of the exciting light, recorded before, by this scattered signal provides the correction function for the emission spectra.

In this experiment a halogen tungsten lamp is used as standard lamp. The wavelength distribution of its light (voltage of 4.00 V) can be approximated by that of a black body of 1900 K. The wavelength distribution of intensity for this color temperature has to be calculate from Planck´s formula.

$$\rho(\nu)\ d\nu = \frac{8\pi h \nu^3}{c^3} \frac{1}{\exp(\frac{h\nu}{kT}) - 1}\ d\nu$$

as photon flux in dependence on wavelength i(λ)dλ.

$$i(\lambda)d\lambda = -\frac{8\pi}{\lambda^4} \frac{1}{\exp(\frac{hc}{\lambda kT}) - 1} d\lambda$$

One obtains the correction function for emission spectra by dividing the calculated distribution by the measured spectrum.

V.2. Inner Filter Effects

The apparent emission intensity and spectral distribution can dependent on the optical density of the sample and the precise geometry of sample illumination. The path length of exciting light through the sample to the point observed by the detection channel and the path length of the emission light through the sample determine the influence of the absorption behavior on excitation and emission spectra.

If there is a strong overlap of absorption and emission spectra (the so-called reabsorption, if the absorbing and emitting species are the same) one often observes a reduced emission intensity at blue side of the emission spectrum. In general, the influence of the absorption on the emission spectrum is call Post Filter Effect.

In excitation spectroscopy a high optical density at excitation wavelength can reduce the exciting intensity in the observed volume element. As a result one might measure a smaller emission intensity compared to a sample with a smaller optical density (Pre Filter Effect).

The correction of these effects is a complicated problem, since one needs the exact description of the geometrical light paths in the sample and the spectral characteristics of the probe.