Cathodoluminescence characterization of organic semiconductor materials for light emitting device applications

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We report the development of a cathodoluminescence-based characterization technique for the investigation of organic semiconductor materials for organic light emitting device (OLED) applications. While photoluminescence is known to predominantly address singlet exciton excitation and recombination processes, cathodoluminescence is able to simultaneously probe singlet and triplet exciton dynamics which is of importance for electroluminescence. Especially, in the case of the so-called triplet harvester materials, the generation of triplet excitons during cathodoluminescence opens the way for materials characterization without OLED device operation. Since singlet and triplet excitons are created simultaneously, as in the case of OLED operation, we compare PL, electro luminescence (EL), and CL spectra from OLED materials. We demonstrate how CL may complement PL in the case of triplet harvester materials characterization, without test device fabrication.

I. INTRODUCTION

Since the presentation of the first organic light emitting diodes (OLEDs) by Tang and VanSlyke1 in 1987 and Burroughes et al.2 in 1990, conjugated small molecules and polymers, respectively, have gained much interest in materials research as well as device development. To a certain amount, materials characterization and quality control can be achieved using photoluminescence (PL) prior and subsequent to device processing. A main problem with PL, however, is that laser excitation is only able to generate singlet excitons. Triplet excitons, which are additionally created with a probability of 75% by the charge carrier injection process during OLED device operation, cannot be addressed. This is a major drawback, especially for materials exhibiting the so-called triplet harvester molecules for the enhancement of radiative recombination quantum efficiency.3 In this case, PL studies address only the triplet emitter luminescence arising from singlet state (S) of the host material to triplet state (T) of the triplet harvester molecule during intersystem crossing. In this work, we present cathodoluminescence (CL) studies of organic semiconductor materials based on conjugated polymers and small molecules. We probe direct material properties, such as singlet and triplet excitation and recombination dynamics, as experienced during real OLED device operation. Since singlet and triplet excitons are created simultaneously, as in the case of OLED operation, we show that CL allows real material characterization without the need to fabricate OLED test devices.

The paper is organized as follows. In Sec. II, some general aspects of CL are discussed. The application of this well established technique for inorganic luminescent materials to organic luminescent materials is explained. Special emphasis is put on alteration caused by the exciting electron beam which impacts the polymers and small molecules. In Sec. III we compare PL, electro luminescence (EL), and CL spectra from OLED materials. We demonstrate how CL may complement PL in the case of triplet harvester materials characterization, without test device fabrication.

II. EXPERIMENTAL PROCEDURE

A. General aspects of CL

During cathodoluminescence some electron-hole pairs (or for organic semiconductors, some excitons made of negatively and positively charged polarons) are generated within the material under investigation. This appears during deceleration of the exciting electron beam. Other possible energy loss mechanisms are electron backscattering, generation of the so-called secondary electrons, and x-ray emission. In the case of inorganic semiconductor materials, a simple equation is used to calculate the energy necessary to create an exciton,

\[ E_{\text{exciton}} = 2.8E_g + M \]  

in which \( E_g \) is the electronic band gap and \( M = (0, \ldots, 1) \) eV is a material specific constant. During deceleration the incident \( e^- \) beam traverses random paths and the area of the deposited energy becomes pearlike shaped. The average penetration depth \( K_e \) is calculated from Ref. 4,
TABLE I. Calculated $e^-$-beam penetration depth $T_e$ using Eq. (2). Mass density data for Si, GaAs, GaN, and ZnSe are taken from Madelung (Ref. 12). In the case of C–H-based polymers, typical textbook values for amorphous and crystalline morphology are taken from Brandrup and Immergut (Ref. 13).

<table>
<thead>
<tr>
<th>Material</th>
<th>Density $\rho$ (g/cm$^3$)</th>
<th>Calculated $R_e$ ($\mu$m) at 5 kV</th>
<th>Calculated $R_e$ ($\mu$m) at 10 kV</th>
<th>Calculated $R_e$ ($\mu$m) at 20 kV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>2.33</td>
<td>0.29</td>
<td>0.96</td>
<td>3.2</td>
</tr>
<tr>
<td>GaAs</td>
<td>5.32</td>
<td>0.13</td>
<td>0.42</td>
<td>1.4</td>
</tr>
<tr>
<td>GaN</td>
<td>6.09</td>
<td>0.11</td>
<td>0.37</td>
<td>1.2</td>
</tr>
<tr>
<td>ZnSe</td>
<td>5.27</td>
<td>0.13</td>
<td>0.43</td>
<td>1.43</td>
</tr>
<tr>
<td>Typ. C–H-based polymer (range)</td>
<td>0.8 (…1.3)</td>
<td>0.8</td>
<td>2.8</td>
<td>9.4</td>
</tr>
<tr>
<td>Typ. F–H-based polymer (range)</td>
<td>2.0 (…2.2)</td>
<td>0.33</td>
<td>1.1</td>
<td>3.8</td>
</tr>
<tr>
<td>Typ. C–H–/F–H-copolymer (range)</td>
<td>1.7 (…1.8)</td>
<td>0.40</td>
<td>1.3</td>
<td>4.4</td>
</tr>
</tbody>
</table>

$R_e(\mu m) = (0.0398/\rho)U_B^{1.75}$,

where $\rho$ and $U_B$ are the materials density (g/cm$^3$) and electron beam acceleration voltage (kV), respectively. In Table I an overview on typical values of calculated $R_e$ values is given for some important inorganic semiconductor materials and typical polymers. The exciton generation rate $g$ can be derived from

$g = U_B I_B(1 - f)/E_{\text{exciton}}$,

where $I_B$ and $(1 - f)$ are the $e^-$-beam current and fraction of deceleration energy converted into excitons, respectively. For a review of cathodoluminescence characterization focusing on inorganic semiconductor materials, see, e.g., Yacobi and Halt and references therein.

B. CL setup

The CL experiments presented in this work were carried out at room temperature in a JEOL JSM 6400 scanning electron microscope ($U_{\text{max}} = 40$ kV, $I_{\text{max}} = 1$ $\mu$A), equipped with a Zeiss DSM 940/962 mirror and a waveguide system for light extraction. Spectrally resolved measurements were performed using a 0.25 or 0.35 m monochromator and a silicon based detector. Time-dependent CL studies were done using a beam blanking setup (time resolution <1 $\mu$s) and cumulating the whole CL light with a photomultiplier tube (time response: <1 ns).

C. Application of CL to organic semiconductor films

A prerequisite for CL studies is that the sample under investigation is conducting. For that reason, the small molecule or polymer layers were deposited on graphite plates with mirrorlike surface. However, even in this case, under $e^-$-beam exposure, the conjugated organic semiconductor materials investigated showed unstable behavior: After turning on the $e^-$ beam, the luminescence intensity dropped rapidly to nonmeasurable small values, which is attributed to the destruction of the molecules after intense $e^-$-beam exposure. To suppress this effect, we developed a procedure where the sample is continuously moved during $e^-$-beam excitation. Typical speeds of $x$ or $y$ translation were in the order of 0.1 mm/s and, as a result, well pronounced luminescence spectra could be acquired [Fig. 1(a)]. After a minimum movement is kept, a constant luminescence signal height is found and, in this case, no $e^-$-beam induced material alteration affects the measurement process.

Please note: Structural transformations of polymers using incident high energy electrons are widely used for $e^-$-beam lithography. Polymethylmethacrylate (PMMA), for instance, is often used as resist (see, e.g., Ref. 5). After $e^-$-beam irradiation the long polymer chain breaks into short fragments which are later dissolved in solvents. In this work, under continuous $e^-$-beam excitation without sample movement, time dependent CL measurements exhibited material alteration with decay time varying from 1 ms for the conjugated small molecule Zn(BOX)$_2$+4.9% Ir[ppy]$_3$ (CL setting: $U_B = 10$ kV, $I_B = 3$ nA) to 10 ms for the conjugated polymer poly-phenylene-vinylen (PPV) (CL settings: $U_B = 17$ kV, $I_B = 3$ nA), respectively (see Table II). For details on the chemical nature of the materials it is referred to Sec. II E. In this work, all exciton recombination lifetimes were shorter than 1 $\mu$s (time resolution limit of the setup), showing that the recombination process is much faster than the $e^-$-beam induced material alteration. As a consequence, no impact of $e^-$-beam induced material alteration or similar effect of the sample movement speed on the CL spectra was observed. This establishes sample movement as a reliable measurement procedure to determine CL spectra of organic semiconductor materials which rapidly degrade under $e^-$-beam exposure.

![FIG. 1. (a) CL spectra of a polyfluorene blend organic semiconductor under a varying electron acceleration voltage carried out at room temperature. (b) Comparison of EL, PL, and CL spectra carried out for the small molecules OLED material Zn-Box+1% of Ir[ppy]. For comparison the spectra were normalized to the same peak intensity.](image-url)
TABLE II. Degradation of (a) PPV and (b) Zn(BOX)₂, under continuous e⁻-beam excitation without sample movement. The lifetime was defined as the time after which the initial luminescence intensity dropped by the factor 1/e. Note: Beam blanking opens and closes at τ<1 μs.

<table>
<thead>
<tr>
<th></th>
<th>PPV</th>
<th>Zn(BOX)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recombination</td>
<td>e⁻-beam induced</td>
<td>e⁻-beam induced</td>
</tr>
<tr>
<td>lifetime (PL)</td>
<td>17 keV,(4,...,8) nA</td>
<td>10 keV,(1,...,8) nA</td>
</tr>
<tr>
<td>EL drop</td>
<td>1 ms±0.2 ms</td>
<td>(18,...,8) ms±2 ms</td>
</tr>
</tbody>
</table>

D. Photoluminescence and electroluminescence setup

PL measurements were carried out in a closed cycle cryostat (T=15,…,330 K) using an argon ion laser (λ =350 nm or λ=360 nm, P=1,…,50 mW), a 0.25 m monochromator, a photomultiplier tube as detector, and a lock-in amplifier. In the case of EL, the laser excitation source was replaced by an electrical pulse generator.

E. Materials under investigation

As conjugated polymers we investigated PPV as well as polyfluorene-based blend layers, with 200 nm–1.5 μm thickness, deposited by spin coating.

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Every time electrically conducting graphite substrates were used, with a mirrorlike surface.

III. RESULTS AND DISCUSSION

A. General aspects

In Fig. 1(a) we plot a series of CL spectra collected on a polyfluorene blend (thickness 1.6 μm) versus e⁻-beam acceleration voltage (Uₜ=5,…,40 kV) at constant e⁻-beam current (I=0.1 nA). Up to 25 kV the CL intensity increases due to a rising exciton generation rate [Eq. (3)]. The shape of the CL spectra does not change with increasing excitation density, which is an important issue for reproducible material studies. However, above 25 kV [not shown in Fig. 1(a)] the CL intensity drops. This comes from a too great e⁻-beam penetration depth which causes a major energy deposition, below the polymer layer, in the graphite substrate.

In Fig. 1(b) we plot CL, PL, and EL spectra of Zn(BOX)₂+1% Ir[ppy]₃. For comparison purpose, all spectra were normalized to the same central peak height. In all three cases a well pronounced double luminescence peak, related to the fluorescent triplet exciton transition of the Ir[ppy]₃ dye dopant is visible around 510 and 535 nm, respectively. In the case of CL, the spectrum is slightly shifted to greater wavelength and in addition, a triple peak seems to develop. Both effects are artifacts of the CL sampling setup. Indeed, the waveguide used to transfer the luminescence from the scanning electron microscope (SEM) interior to the external spectrometer causes a superposition of light beams with varying reflection angles. Focused on the spectrometer entrance slit, this creates the change of CL spectrum compared to PL and EL. Another possible explanation for the small differences in spectrum shape of PL, EL, and CL is a difference in luminescence light reabsorption in the organic layer, because the exciton distribution may slightly differ between the three excitation techniques. In the case of PL, notice in addition the singlet exciton luminescence peak of the Zn(BOX)₂ host at 455 nm is also visible which is only slightly excited in EL and CL (peak shoulder position at approximately 440 nm). The difference in occurrence is related to the different generation rates of singlet and triplet excitons in PL (100% single excitons) and EL or CL (25% singlet and 75% triplet excitons).

To summarize the comparison of the luminescence techniques: CL can be carried out to provide materials information similar to EL and PL; the minor differences observed in the spectra shapes are related either to the different spectrometer setup used in CL, PL, and EL or to the range of excitation density (i.e., number of singlet versus triplet excitons).

The e⁻-beam current density dependence of the CL intensity has been checked on a 200 nm thick OLED copolymer [Fig. 2(a)]. The electron acceleration voltage was set to 15 kV, while the current was changed from 0.1 nA to 1.0 μA. From Eq. (3), we know that the CL signal intensity should follow linearly with excitation current. This is not found. The CL signal increases very weakly (sublinearly) with current up to 0.1 μA but, between 0.1 and 1.0 μA, a CL signal saturation is observed. This deviation is related to electrical charging of the samples, due to a too low polymer conductivity. Charging the layer causes a build up...
of an electrical field which is opposite to the $e^-$-beam acceleration voltage and reduces the effective value.

Similar variations of the acceleration voltage were carried out from 1 to 40 kV at fixed current of 100 nA on the same 200 nm thick OLED copolymer layer [Fig. 2(b)]. At 100 nA the CL signal is close to the saturation regime. Figure 2(b) shows that the CL intensity significantly increases in the low voltage regime ($U_B < 20$ kV) and slowly decreases above this value. For $U_B < 20$ kV an increase of $U_B$ corresponds to a larger number of generated excitons in the polymer layer while, at $U_B > (25, ..., 30)$ kV, the majority of electrons step into the graphite substrate. The theoretical acceleration voltage with optimum penetration depth that corresponds to the layer-substrate interface of 200 nm is considerably higher than the experimental voltage at which the CL signal starts to decrease again. Using Eq. (2) to calculate the average penetration depth $R_e$, we find that $R_e$ is equal to the layer thickness (200 nm) at $U_B = 3.4$ kV. For the materials density of the copolymer we used the average polymer value of 1.7 g/cm$^3$ from Table I. The great deficiency is related to the layer charging, which causes a reversal electrical field, as already discussed for the measurement in Fig. 2(a). This indicated that the exciton generation model found for inorganic materials (see Sec. II) applies only to organic semiconductor materials, when sample charging effects are taken into account.

B. Application to triplet harvester materials: Comparison of CL with PL  

In this part we discuss the application of CL to the exploration of triplet harvester light emitting materials. We focus on Alq$_3$/PtOEP and show in Fig. 3 the electron transition scheme of this host/guest material system.7,8

In the case of PL electrons are excited from the $S_0$ ground level to some $S_1$ or related excited state $S''$ of the Alq$_3$ host material forming a singlet exciton. Excitation of the triplet excitons or intercrossing of the host singlet with host triplet states is quantum mechanically forbidden. Singlet excitons, however, may be transferred to the PtOEP guest molecules ($S_{1,host} \rightarrow S_{1, guest}$) as a result of the so-called Förster energy transfer (FET). Then they can undergo $S_{1, guest} \rightarrow T_{1, guest}$ intersystem crossing, due to the pronounced spin-orbit coupling in the PtOEP molecule (Fig. 3). In this case, in photoluminescence (Fig. 4) one observes the broad $S_{1, host} \rightarrow S_{0, host}$ singlet transition centered at about 516 nm, the narrow $T_{1, guest} \rightarrow S_{0, guest}$ triplet transition at 650 nm, and, in addition, a second narrow peak at 622 nm. The latter may come from $S_1 \rightarrow S_0$ singlet transition related to porphyrins not bound in a PtOEP metal complex.9–11 The presence of such “free” porphyrin comes from the PtOEP deposition process and, to a certain extent, can be used to “monitor” the $S_1 \rightarrow S_0$ singlet transition of the guest material which should be invisible in luminescence.9–11 Characteristic of the long range FET from the Alq$_3$ host to the PtOEP guest is that this dipole-dipole-type energy transfer does not depend on the wave function overlap of the host exciton with the guest molecule and should be independent of the exciton density.

![Graph showing dependence of integral CL intensity on electron beam current and acceleration voltage](image)

**FIG. 2.** (a) Dependence of integral CL intensity of 200 nm thick organic semiconductor films on (a) the $e^-$-beam current (under fixed $e^-$-beam acceleration voltage) and (b) the $e^-$-beam acceleration voltage (under fixed $e^-$-beam current).

![Electron transition scheme for Alq$_3$/PtOEP host/guest material blend](image)

**FIG. 3.** Electron transition scheme for an Alq$_3$/PtOEP host/guest material blend. The long range Förster energy transfer of singlet excitons from host to guest molecules occurs also during photoluminescence. Short range Dexter energy transfer of triplet excitons from host to guest appears only when using CL. The short range Dexter energy transfer efficiency depends on the triplet exciton density in the host/guest blend.

![PL spectra collected for laser excitation power of 20, 6.3, 2, 0.4, and 0.04 mW](image)

**FIG. 4.** PL spectra collected for laser excitation power of 20, 6.3, 2, 0.4, and 0.04 mW. The spectral shape does not change with power. At the lowest laser power (0.04 mW) the measurement intensity is close to the signal to noise limit of the setup.
Indeed, the relative ratios of the three photoluminescence transitions do not change with laser excitation intensity (see Fig. 5).

In CL, similar to OLED, singlet and triplet excitons can be excited during e−-beam exposure of the Alq3 host material. In addition to the energy transfer mechanisms effective during PL, triplet excitons may now be transferred from the host to the guest \(T_{1,\text{host}} \rightarrow T_{1,\text{guest}}\). This so-called Dexter energy transfer (DET) is of short range nature and depends on the Alq3 host exciton wave function overlap with the PtOEP guest molecules. Hence, there should be a strong impact on the efficiency of this energy transfer on the value of the e−-beam excitation current which determines the generated singlet and triplet exciton density. Indeed, in Figs. 6 and 7 we observe that when increasing the e−-beam excitation current a strong (relative) increase of the PtOEP guest triplet \(T_{1,\text{guest}} \rightarrow S_{0,\text{guest}}\) luminescence transitions at 654 nm occur compared to the porphyrin guest singlet \(S_{1,\text{guest}} \rightarrow S_{0,\text{guest}}\) transition at 624 nm. Please note: The guest material singlet \(S_{1} \rightarrow S_{0}\) (guest porphyrin) and triplet \(T_{1,\text{guest}} \rightarrow S_{0,\text{guest}}\) (guest PtOEP) transitions are slightly shifted to larger wavelengths, i.e., from 622 to 624 nm and from 650 to 654 nm, respectively, which is attributed to the measurement setup [see Sec. III and discussion of EL, PL, and CL spectra comparison in Fig. 1(b)]. In the case of the CL study the broad Alq3 host singlet \(S_{1,\text{guest}} \rightarrow S_{0,\text{guest}}\) transition observed in PL at 516 nm is separated in two lines: 521 and 530 nm, respectively. In the frame of this work, we have not further followed this observation.

These results on host to guest triplet excitons transfer \(T_{1,\text{host}} \rightarrow T_{1,\text{guest}}\) imply that the CL technique is a powerful one to study luminescent organic semiconductor materials. An advantage is that the materials evaluation can be carried out without OLED device fabrication. Moreover, similar to EL device operation, pure materials properties will be addressed without any complex, nonoptimized device design interference effect.

IV. SUMMARY AND OUTLOOK

We have presented a CL investigation of organic semiconducting materials for OLED applications. We have shown that e−-beam excitation is able to create singlet and triplet excitons similar to the carrier injection of an OLED device. As an example, we presented a comparison of PL and EL study of the so-called triplet harvester system Alq3/PtOEP where the transfer of Alq3 host material triplet excitons to the PtOEP guest molecule can be observed. This opens the way for materials studies of efficient organic semiconductor luminescent materials for operation in OLEDs without any need of test device fabrication.

Future studies should include time dependent CL studies of triplet harvester materials where the various radiative recombination processes of host singlet, guest singlet, and guest triplet excitons may be separated due to their different recombination lifetime: triplet exciton recombination (phosphorescence) exhibiting a longer lifetime compared to singlet exciton recombination (fluorescence).

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FIG. 5. Integrated photoluminescence signal vs excitation power for different host and guest material transitions. The slope 1 in the double logarithmic plot suggests the absence of pronounced nonradiative recombination processes.

FIG. 6. CL spectra as a function of the e−-beam excitation current. The evolution of the host singlet, guest porphyrin singlet, and guest triplet transitions are shown in Fig. 7.

FIG. 7. CL peak intensity dependence of the host singlet, guest porphyrin singlet, and guest triplet transitions versus e−-beam current.