# Recombination Radiation from Organic Solids

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**Summary:** The recombination radiation from organic solids, defined as the light emission following the fusion of oppositely charged carriers into an electrically neutral state, is discussed as a phenomenon underlying the function of organic light-emitting diodes (LEDs). Its intensity and spectral range depend on the population and nature of the emissive states, which differ, in general, from those created using light. These differences are pointed out and shown to be a result of the reverse pathways of the mutual transformation of localized molecular excitons and coulombically-correlated charge-pair excited states formed either by photoexcitation or electron-hole recombination. Spectral features of the radiation produced by the recombination of statistically independent charge carriers are discussed in terms of two molecules-based excited states like *excimers* or *electromers* in single-component materials and *exciplexes* or *electroplexes* in multicomponent materials. Consequences for optical and electrical characteristics of organic LEDs are discussed and illustrated by examples. Progress in the fundamental and applied research may be expected based on properties of recombination-produced electronic excited states.

**Keywords:** charge recombination processes; electronically excited states; organic electroluminescence; organic light-emitting diodes; recombination radiation

## Introduction

The oppositely charged carriers (e.g. holes and electrons) recombining (or combining) in an organic solid release a considerable amount of energy which can be emitted in the form of electromagnetic radiation. This is called *recombination radiation*. If electrons and holes are injected from electrodes applied to a layer or a system of layers of organic materials, we deal with *organic recombination electroluminescence* (EL) and the devices are called *organic light-emitting diodes* (LEDs).[1] Due to their wide-spectrum display performance, improved stability and relatively simple device architecture, organic LEDs show advantages compared with conventional inorganic semiconductor materials.[2,3] Worldwide efforts in their commercialization

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are one of the most important reasons making recombination radiation in organic solids a hot scientific topic. Analyses of fundamental processes of charge injection and transport, and properties of emissive states underlying organic LED operation mechanisms enable better understanding of the recombination processes and form a firm basis for tailoring organic EL devices.

In the present paper, the processes governing the recombination radiation in organic solids are discussed with particular attention paid to recombination mechanisms and the nature of emissive states produced in the electron-hole recombination process.

## Types of Charge Recombination

The charge recombination process can be defined as fusion of a positive (e.g. hole) and a negative (e.g. electron) charge carrier into an electrically neutral entity or, following its evolution, successive excited states. The *initial* (or geminate) (IR) and *volume-controlled* (VR) recombination can be distinguished on the basis of the charge-carrier origin (Fig. 1).[4]

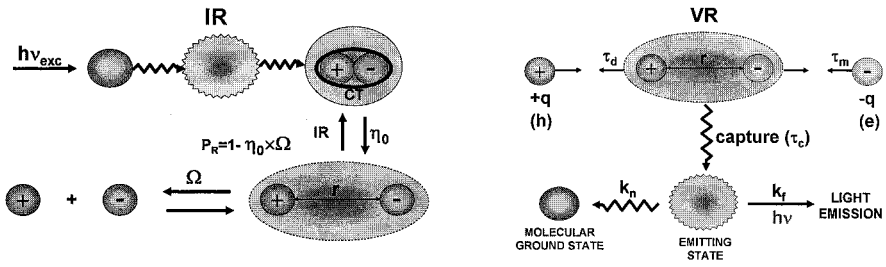



Figure 1. Initial (IR) and volume-controlled (VR) recombination (for explanation, see text).

The IR is the recombination process following the initial carrier separation, from an unstable, locally excited state, forming a nearest-neighbor charge-transfer (CT) state. It typically occurs as a part of intrinsic photoconduction in organic solids due to generation of charge from light-excited molecular states. The probability ($P_{IR}$) of the IR can be expressed by the primary (often assumed to be electric field-independent) quantum yield in carrier pairs for the absorbed photon, $\eta_0$, and the (e...h) pair dissociation probability, $\Omega$, $P_{IR} = 1 - \eta_0\Omega$. The electric field effect on the effective

charge separation can be observed in generation-controlled photoconduction or electric field-induced quenching of luminescence since the external electric field-enhanced dissociation decreases the number of emitting states.[5]

If the oppositely charged carriers are generated independently far away from each other (for example, injected from electrodes), the VR takes place, and the carriers are statistically independent of each other, the recombination process is kinetically bimolecular. It naturally proceeds through a coulombically-correlated electron-hole pair (e...h) leading to various emitting states in the ultimate recombination step (mutual carrier capture). The capture probability is defined by $P_R^{(2)} = (1+\tau_c/\tau_d)^{-1}$, where $\tau_c$ and $\tau_d$ is the capture and dissociation time, respectively. The classic treatment of carrier recombination can be related to the notion of the recombination time. The recombination time is a combination of the carrier motion time ($\tau_m$), i.e. the time to get the carriers within the capture radius (it is often identified with the Coulombic radius $r_C = e^2/4\pi\varepsilon_0\varepsilon kT$), and the elementary capture time ($\tau_c$) , $\tau_{rec}^{-1} = \tau_m^{-1} + \tau_c^{-1}$. Following the traditional description of recombination processes in ionized gases, a Langevin-like and Thomson-like recombination[4,6] can be defined if $\tau_c << \tau_m$ and $\tau_c >> \tau_m$, respectively (cf. Fig. 2).

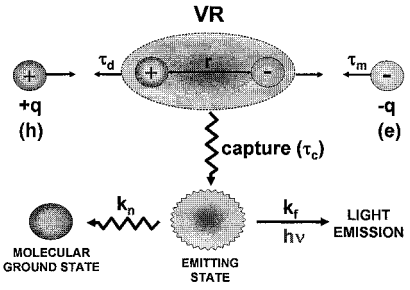



Figure 2. VC recombination scheme allowing to distinguish between Langevin and Thomson recombination (for explanation, see text).

In solid state physics, these two cases have been distinguished by comparison of the mean free path for optical phonon emission with the average distance across a sphere of critical radius $r_c$.[7] A signature of the Langevin recombination mechanism is a field and temperature independence of the bimolecular recombination rate constant ($\gamma_{eh}$) of the effective mobility ($\mu_m$) ratio. This is often the case (especially for low electric fields). However, as we will see later on, it becomes a field-

dependent process at higher electric fields, suggesting the Thomson-like recombination to set in.

## The Nature of Excited States

A variety of emissive states can be created either by photoexcitation or a charge carrier recombination process. Let us first consider a simpler case of single-component organic solids (Fig. 3). A molecular (well-localized) excited state is a typical product of photoexcitation. Light absorption creates excited molecular singlet ($M_S^*$) which can relax by the intersystem-crossing to an excited molecular triplet ($M_T^*$). Their radiative decay produces fluorescence and phosphorescence. On the other hand, the interaction of an excited molecular state with a ground-state molecule leads to the formation of locally-excited *excimer* or *charge-transfer excimer* if the distance between molecules is shorter than 0.4 nm. If it is larger than 0.4 nm, one can deal with direct transition of a LUMO-located electron of one molecule to HOMO-located hole of another molecule (cross-transition); such an "emitting state" has been called *electromer*. Electromer emission occurs when, due to a defect or disorder, the electron transfer from LUMO to LUMO is impeded. The level shift makes the emission red-shifted with respect to the molecular emission as well as to the excimer emission. It is important to note that "electromer" emission requires the charge carriers to be separated, for example by the autoionization process.

In the volume recombination process, such separated charge pairs (e...h) are formed when statistically independent carriers approach each other. Again, molecular and bimolecular excited states can be created. The difference between these two ways of creation of emissive states is clearly apparent. The charge pair states, as a rule, precede final emissive states under recombination and follow the localized states under photoexcitation. This is a good reason for expecting the bimolecular excited states to be produced more efficiently in the charge recombination process. Thus, the emission spectrum is expected to be different or at least more complex than that under photoexcitation. There are few striking examples confirming this expectation. In Fig. 4 we see the photoluminescence spectrum (PL) of an amine derivative (TAPC) in polycarbonate with its recombination radiation spectrum (EL).

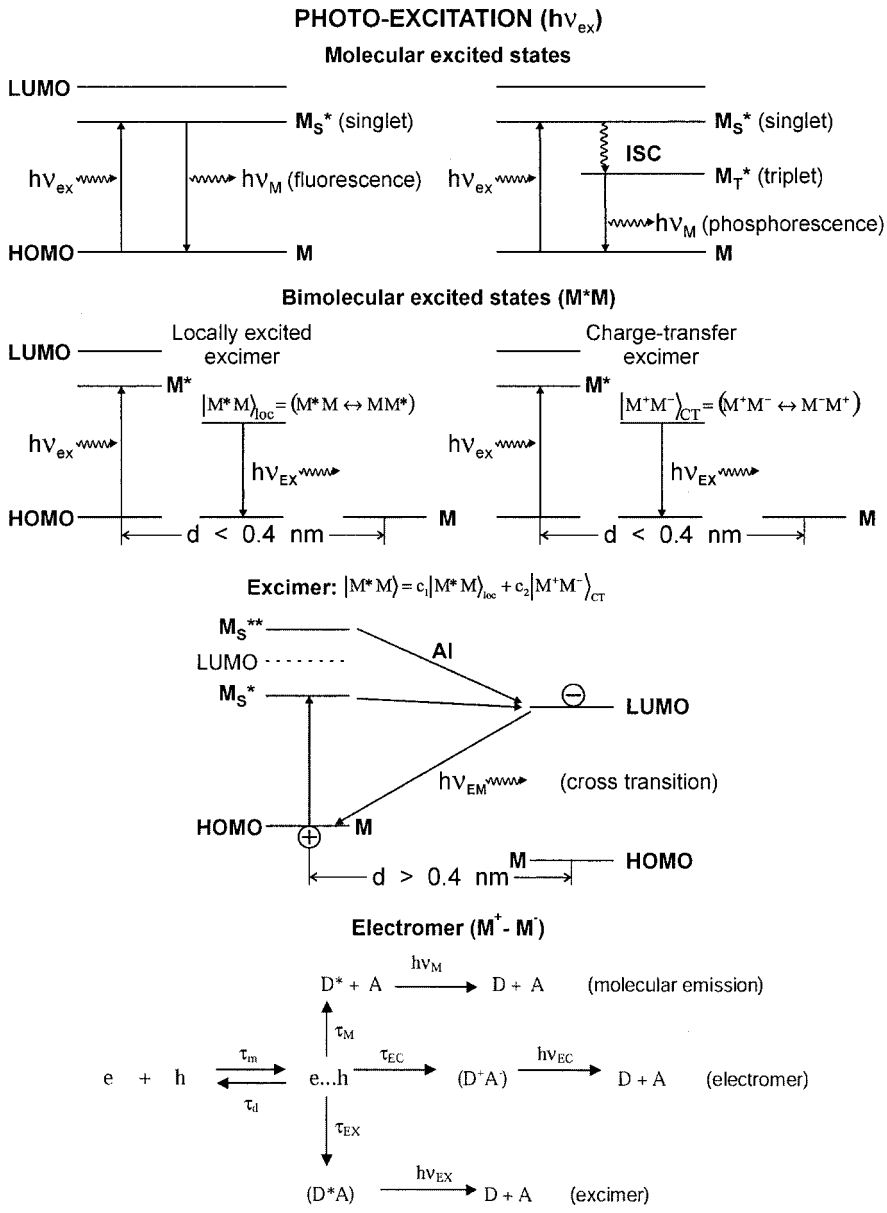
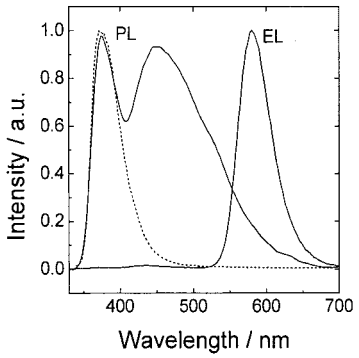
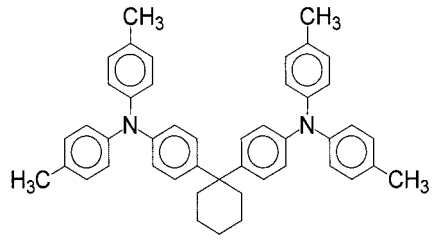



Figure 3. Photoexcited and electron-hole recombination-produced excited states in single-component organic solids.




1,1-Bis[4-(di-p-tolylamino)phenyl]cyclohexane
(TAPC)

Figure 4. Optically excited (PL) and recombination radiation (EL) spectra of TAPC thin films. The dashed curve is the PL spectrum of TAPC in a $10^{-5}$M dichloromethane solution.[8]

While in the photoexcited spectrum the molecular emission combined with red-shifted band of the excimer emission is apparent, in the recombination radiation only a single strongly red-shifted emission band could be detected and ascribed to the electromer states. Another striking example of the difference between photoexcited and charge recombination-generated emission spectra is due to anthracene (Fig. 5).

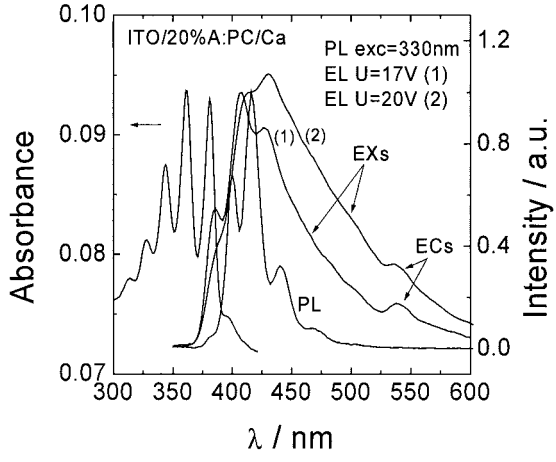



Figure 5. Optically excited (PL) and recombination (EL) emission from anthracene (A) dispersed in polycarbonate (PC). EXs denotes emission from excimers, ECs emission from electromers. Absorbance of the 20%A:PC film is shown for comparison.[9]

Again, the PL spectrum is dominated by the emission from the molecular states, the recombination radiation (EL) reveals the broad band of a series of excimers (EXs) and electromers (ECs). The latter are completely absent in the PL spectrum. One could argue that the longest-wavelength maximum in the EL spectra is due to an impurity (e.g. an oxidation product of the compound). Such a possibility, considered earlier to explain a weak emission at 540-550 nm in the thermoluminescence of γ-irradiated anthracene in squalane,[10] has been, however, questioned on the basis of time-resolved experiments. Nevertheless, this point as well as the recombination of dimer cations with the anion[11] still requires further studies.

In the case of two- or multicomponent materials with different ionization potentials and electronic affinities, the situation becomes more complex. Let us take a look at the two-component system displayed in Fig. 6.

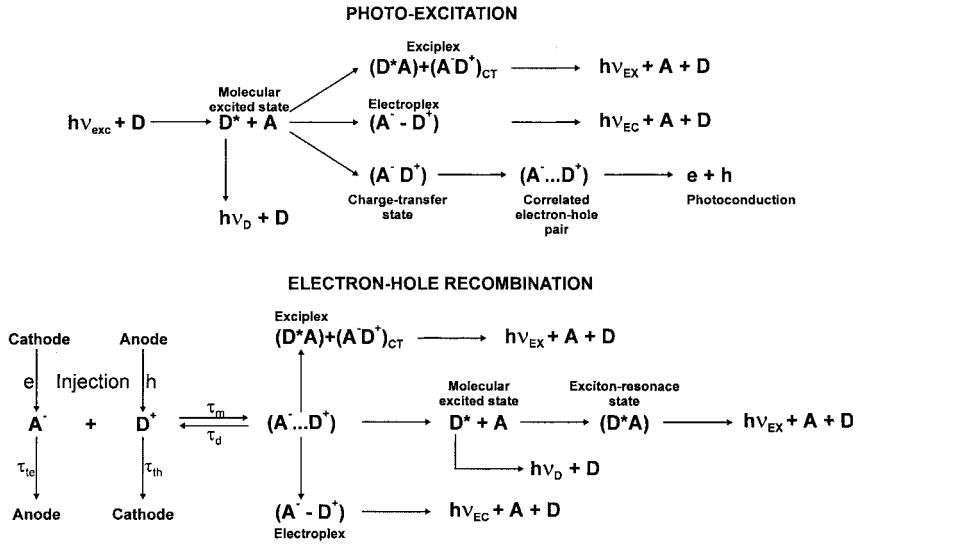



Figure 6. Excited states in two-component [electron donor (D) – electron acceptor (A)] system formed under photoexcitation and in the electron-hole recombination process.

Light absorbed by, say, electron donor molecules produces excited donor singlets (D*). Their radiative relaxation shows up as donor fluorescence ($h\nu_D$). Interacting with the ground-state electron acceptors, they can form exciplexes and *electroplexes*, the latter being two different molecule, analogue of electromers in single-component solids.

## Organic Electroluminescence

If the recombining carriers [e.g. ($A^-$, $D^+$) in an organic acceptor-donor system] are formed by electrons and holes injected from electrodes as shown in Fig. 6, we deal with recombination electroluminescence (EL). In Fig. 7 an example of one of the most efficient double-layer device allowing observation of organic EL is presented.

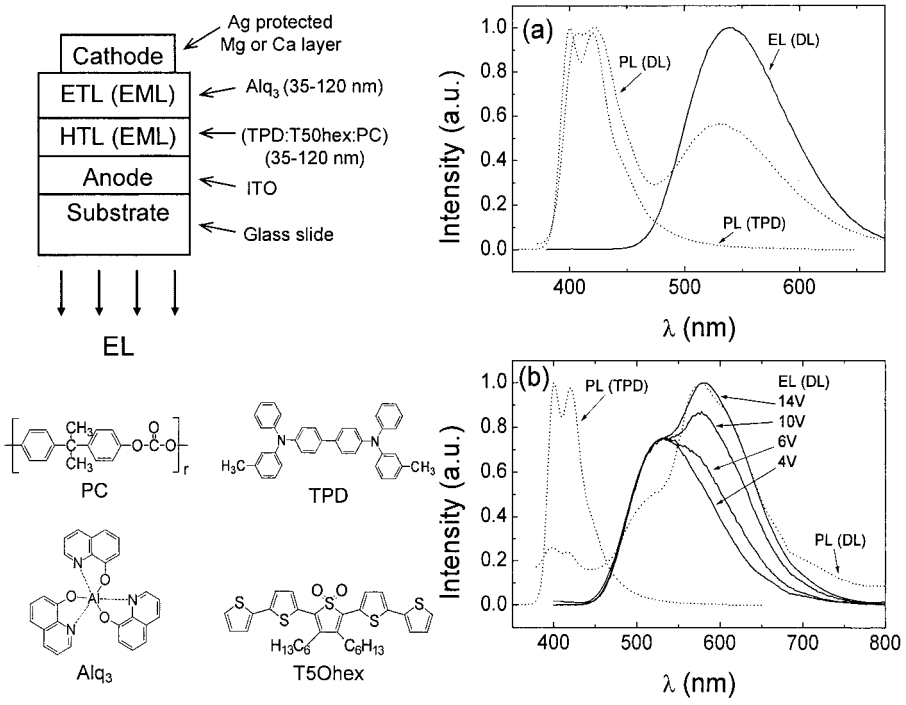



Figure 7. A double-layer (DL) organic LED and its EL spectra as compared with the PL spectra of the component materials.[12]

Electrons injected from cathode are transported through an electron-transporting layer (ETL), holes injected from anode are transported through a hole-transporting layer (HTL). Their recombination can occur either in the ETL, HTL or both. Then, different excited states are produced and the emission spectrum is expected to be a combination of their emission characteristics. The system consists of the $Alq_3$ electron-transporting layer and a hole-transporting

layer composed of TPD and a thiophene derivative (T5Ohex) dispersed in the polycarbonate matrix. The PL spectrum contains three bands belonging to three different molecules (TPD – blue; $Alq_3$ – green; and T5Ohex – red). Typically, in the EL spectrum the TPD emission disappear and the contribution of two remaining components depends on the electric field: the dominant red emission at high fields disappears at low fields, passing through decreasing proportions at intermediate fields. This is an example showing how the EL emission color can be changed varying only the voltage applied to the device.

Another example is shown in Fig. 8. A mixture of the electron-donor (TPD) and electron-acceptor (PBD) molecules can form a single-layer (SL) system (Fig. 8a) or these molecules can be brought into an intimate contact on the interface of two independent layers; TPD in polycarbonate and 100% evaporated PBD (Fig. 8b). Their emission spectra are different (Figs. 8a, b, bottom).

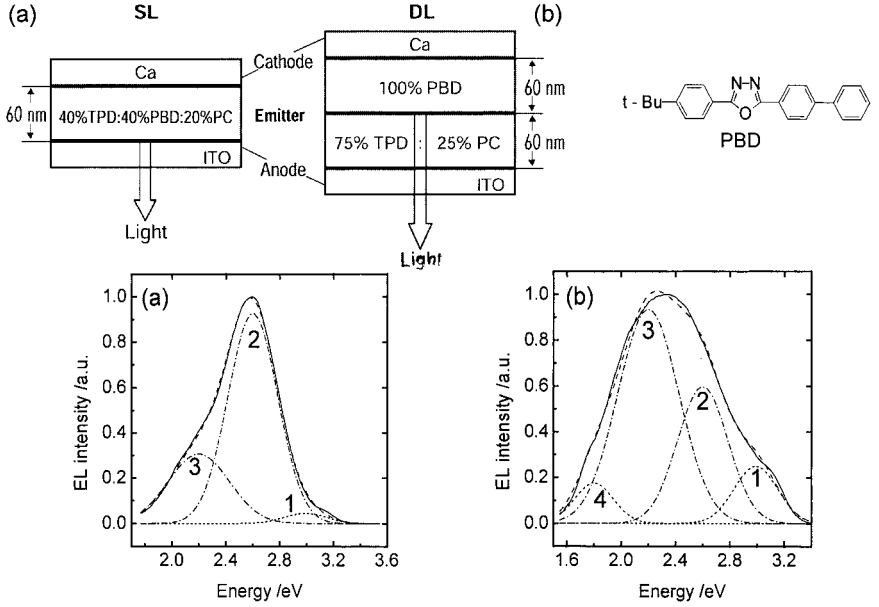



Figure 8. Configuration of the two-component single-layer (SL) (a) and double-layer (DL) (b) LEDs and corresponding EL spectra with their Gaussian profile analysis showing emission from different excited states.[13]

In the SL system a narrower spectrum is dominated by band 2, which in the broader spectrum of the DL system decreases; a slightly pronounced shoulder 3 in the previous spectrum becoming now a dominating feature. This is an excellent example of coexistence of exciplex and electroplex emissions. In the energy level scheme of the active molecules, we can see how they are formed (Fig. 9). The locally excited exciplex is created by a LUMO PBD → LUMO TPD electron transfer, the molecular TPD singlet forming an exciplex with the nearest neighbor molecule of PBD (process 2'). Due to an energy barrier for slightly more distant molecules, a cross transition takes place (process 3). As a result, a red-shifted emission 3 appears in the spectrum. A strong attractive electric field at the TPD/PBD interface impedes the external electric field-assisted charge-pair dissociation, the electroplex component becoming the major feature of the DL system emission spectrum.

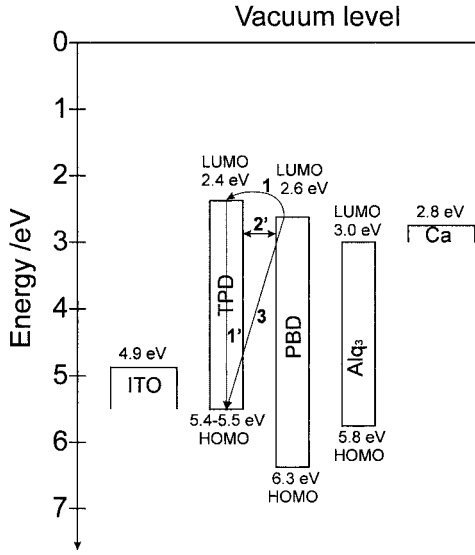



Figure 9. The energy level scheme of the material components used for manufacturing the cells described in Fig. 8. Selected electronic transitions are indicated by lines with arrows.[12]

## EL Quantum Efficiency

From the above it has been clear that single-, double- and even more-layer thin film systems form devices which are called organic light-emitting diodes (LEDs). One of their most important characteristics is the EL quantum efficiency defined as the quantum flux [Φ/<hν>] divided by the

carrier flux [$j/e$] resulting from their driving current, $j$:

$$\varphi_{EL}^{(ext)} = \frac{\Phi/\langle h\nu \rangle}{j/e} \quad (1)$$

where $\langle h\nu \rangle$ is the averaged photon energy.

The common feature of the EL quantum efficiency of organic LEDs is its nonmonotonic evolution with driving current (electric field applied to the device). Typical examples of electrofluorescence efficiencies for a series of organic LEDs are presented in Fig. 10. As a rule, the quantum efficiency increases in the low-field region and decreases above a certain field (usually close to 1 MV/cm); the current-voltage characteristics do not follow the space-charge-limited current pattern. The emitter layer composed of neat or diphenylpentacene (DPP)-doped $Alq_3$ is here placed between the $Alq_3$ electron-transporting layer and TPD hole-transporting layer. DPP forms holes as well as electron traps in $Alq_3$. Their EL quantum efficiency (QE) shows a maximum for a certain field, but its position and width depend on the emitter composition.

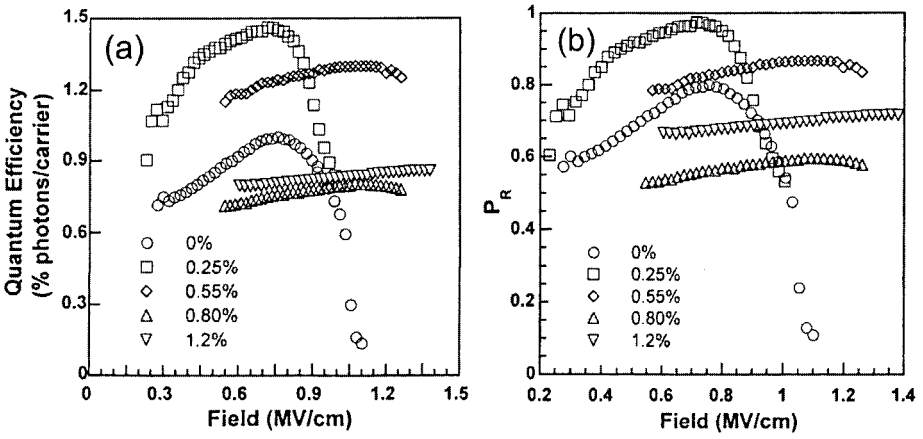



Figure 10. The quantum efficiency (a) and recombination probability, $P_R$, (b) as a function of electric field for the three-layer EL devices ITO/TPD/$Alq_3$:%DPP/$Alq_3$/Mg:Ag with varying concentration of DPP (mol % given in the figures).[14]

The well pronounced maximum for neat and low-doped emitters shifts remarkably and broadens with increasing concentration of DPP.

By definition, the measured QE of EL is proportional to the radiative decay efficiency of the

emissive states ($\varphi_r$) with a series of proportionality coefficients $\xi$, $P_S$, $P_R$,

$$\varphi_{EL}^{(ext)} = \xi P_S P_R \varphi_r \quad (2)$$

$\xi$ is the light output coupling factor responsible for all light losses in the LED structure, $P_S$-probability of formation of a singlet emitting state, and $P_R$ – recombination probability which is the product of the recombination probability due to the carrier motion [$P_R^{(1)}$] and final carrier capture [$P_R^{(2)}$],

$$P_R = P_R^{(1)} P_R^{(2)} = \left(1 + \tau_m/\tau_t\right)^{-1}\left(1 + \tau_c/\tau_d\right)^{-1} \quad (3)$$

Having $\xi$, $P_S$ and $\varphi_r$, the recombination probability can be extracted from the experimental data of the EL quantum efficiency. The results indicate that the maxima in the recombination probability underlie the maxima in the efficiency. From definitions of the recombination and transit times $\tau_{rec}/\tau_t=(8e\mu_h/9\gamma\varepsilon_0\varepsilon)(j_{SCL}/j)$. Assuming for granted the Langevin recombination mechanism, i.e. the mobility $\mu_h$ recombination rate ratio being independent of electric field, we find that the decrease in the $\tau_{rec}/\tau_t$ ratio is due to the fact that the actual current approaches its space-charge-limited behavior: as field increases, $j_{SCL}/j$ decreases, and $P_R$ increases approaching unity. However, exceeding the field ca. 0.8 MV/cm, $P_R$ becomes a decreasing function of electric field. This means either the Langevin formalism breaks down, $\mu_h/\gamma$ increasing as F increases, or $P_R \cong P_R^{(2)}$, i.e. the capture-controlled (Thomson-like) recombination sets in. Increasing electric field reduces the dissociation time $\tau_d$, the $\tau_c/\tau_d$ ratio increases leading to decreasing probability of recombination and, consequently, to a drop in the EL quantum efficiency. We believe the second possibility is correct since electric field-induced quenching of fluorescence[15] and phosphorescence[16] of various luminescent materials have been observed experimentally.

The importance of selection of proper device structure to maximize the EL quantum efficiency from a given type of the emissive states is worth mentioning. Emission from exciplexes is of considerable interest since their spectra can fall in the middle of the visible region while component molecules emit in the violet or even UV region. We have recently shown that the EL quantum efficiency of exciplex emitting diodes can reach its typical value of ca. 1 %

photon/electron for the efficient emitting singlet molecular states, fabricating a DL structure with properly selected electron- and hole-transporting layers (Fig. 11). The exciplex-forming molecules of m-MTDATA and PBD are brought into an intimate contact on the interface of these materials evaporated successively one on the other. The exciplex appears in the green region in contrast to m-MTDATA and PBD which emit in the blue and violet region.

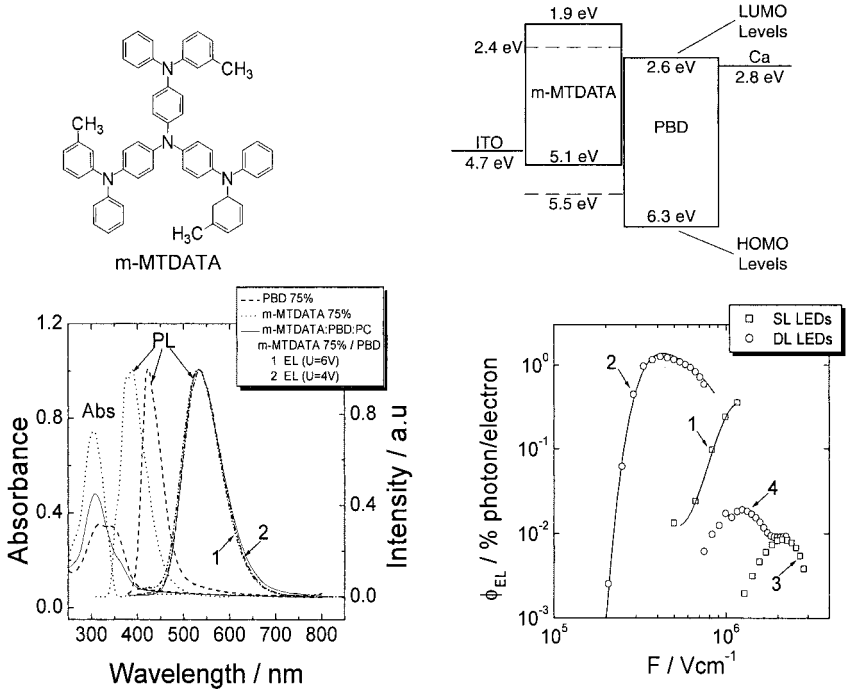



Figure 11. Efficient exciplex emitting diode ITO/m-MTDATA/PBD/Ca. Its composition and energy level scheme of the materials used are shown in the upper part of the figure; absorption, PL and EL spectra together with the field-dependent EL quantum efficiency are shown in the bottom part. Comparison with a LED with a TPD HTL is given (dashed levels in the energy scheme, and curves 3 and 4 for the efficiency).[17]

At a certain field, the QE of EL reaches and even slightly exceeds 1 % photon/electron which is almost two orders of magnitude higher than the (TPD-PBD) exciplex emission efficiency. This is due to a high energy barrier for holes at the m-MTDATA interface as compared with that at the

TPD/PBD interface. We note that this is not the case with a SL structure formed by a mixture of these components. This example shows how, by manipulating the diode structure and selecting proper materials, the desired spectral and performance requirements can be fulfilled.

## Concluding Remarks

Physics of recombination radiation from organic solids reveals some particular spectral features as compared with photoexcited emission. They are associated with a diversity of two-molecular excited states, opening prospects for new ideas in the fundamental research and utilization in practical light-emitting devices.

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[1] J. Kalinowski, *J. Phys. D: Appl. Phys.* **1999**, 32, R179.
[2] J. W. Allen, *J. Luminescence* **1994**, 61/62, 912.
[3] H. Sixl, H. Schenk, N. Yu, *Phys.Bull.* **1998**, 54(3), 225.
[4] J. Kalinowski, *Mol. Cryst. Liq. Cryst.* **2001**, 355, 231.
[5] J. Szmytkowski, W. Stampor, J. Kalinowski, Z. H. Kafafi, *Appl. Phys. Lett.* **2002**, 80, 1465.
[6] J. Kalinowski, M. Cocchi, V. Fattori, P. Di Marco, G. Giro, *Jpn. J. Appl. Phys.* **2001**, 40, L282.
[7] M. Lax, *Phys. Rev.* **1960**, 119, 1502.
[8] J. Kalinowski, G. Giro, M. Cocchi, V. Fattori, P. Di Marco, *Appl. Phys. Lett.* **2000**, 76, 2352.
[9] J. Kalinowski, G, Giro, M. Cocchi, V. Fattori, R. Zamboni, *Chem. Phys.* **2002**, 277, 387.
[10] M. Al-Jarrah, B. Brocklehurst, M. Evans, *J. Chem. Soc. Faraday Trans. 2* **1976**, 72, 1921.
[11] B. Brocklehurst, *Int. J. Radiat. Phys. Chem.* **1974**, 6, 483.
[12] J. Kalinowski, M. Cocchi, G. Giro, V. Fattori, P. Di Marco, *J. Phys. D: Appl. Phys.* **2001**, 34, 2282.
[13] G. Giro, M. Cocchi, J. Kalinowski, P. Di Marco, V. Fattori, *Chem. Phys. Lett.* **2000**, 318, 137.
[14] J. Kalinowski, L. C. Picciolo, H. Murata, Z. H. Kafafi, *J. Appl. Phys.* **2001**, 89, 1866.
[15] W. Stampor, J. Kalinowski, P. Di Marco, V. Fattori, *Appl. Phys. Lett.* **1997**, 70, 1935.
[16] J. Kalinowski, W. Stampor, J. Mężyk, M. Cocchi, D. Virgili, V. Fattori, P. Di Marco, *Phys. Rev. B* **2002**, 66, 235321.
[17] M. Cocchi, D. Virgili, G. Giro, P. Di Marco, J. Kalinowski, Y. Shirota, *Appl. Phys. Lett.* **2002**, 80, 2401.