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Excimers and exciplexes in organic electroluminescence*

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In organic light emitting devices (LEDs) various types of emissive states are created: (i) molecular excited states (localized excitons), or bimolecular (B-M) species: excimers, electromers, exciplexes and electroplexes. The consequences of the formation of B-M excited species for optical and electrical characteristics of organic LEDs are discussed and illustrated by various examples. While molecular excitons can be viewed in some sense as correlated electron–hole (e-h) pairs with the inter-charge mean separation less than an intermolecular spacing, the size of B-M excited states amounts usually to one or two intermolecular spacings. The B-M species can be classified as electrically balanced states, formed under energy and charge exchange between neighbour molecules, and have either a singlet or a triplet character. The focus of the paper is on excimer and exciplex forming single phosphorescent dopant blends-based emitting layers but characteristic features of other B-M excited species (electromers and electroplexes) and their emissions are also mentioned. Of particular interest in modern optoelectronics are white and infrared organic LEDs. It is shown how excimer and exciplex emissions can be employed in manufacturing such devices. Examples include efficient white and near-infrared LEDs, based on single dopant emitters of an efficient N–C–N-coordinated platinum(II) complex phosphor, and their improved versions, obtained by modification of the emitter matrix materials and electron injecting electrodes.

Key words: *organic electroluminescence; organic LEDs; bimolecular excited states; near-infrared; white light emitting diodes*

1. Introduction

Excited states of molecular solids are traceable to properties of individual molecules. However, the energy of weak van der Waals interactions between molecules impose a notable, communal response upon the behaviour of the molecular condensed phase (see e.g., [1, 2]). The collective response is embodied in an entity called an *exci-*

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ton (see Sect. 2). In single component organic solids composed of chemically identical molecules which do not aggregate in the ground state, bimolecular (B-M) excited states are possible due to resonance interactions of a *molecular exciton* with neighbour non-excited molecules (M). They are called *excimers* [3]. Exciton and charge-transfer resonance can be defined by intermolecular exchange of the singlet or triplet excitation energy and/or charge. The first process leads to the so called 'locally-excited excimers' (local excimers), the second to 'charge-transfer excimers' (CT excimers). In general, mixed excimers are formed with different contributions of local and CT excimer structures (see Sect. 3). In bicomponent and multicomponent molecular solids (chemically different molecular mixtures – molecular blends), especially for electron donor (D) and electron acceptor (A) molecules, the formation of bimolecular excited states by electron transfer from donor to acceptor is highly facilitated, in analogy to single-component systems: they are called *exciplexes* [4]. The molecular and B-M excited states can be generated either optically, by light, or electrically, by electron –hole recombination, that is they appear in both photoluminescence (PL) and electroluminescence (EL). An interesting combination of these two emissions has recently been observed and called *electrophotoluminescence* (EL-PL) [5]. In EL, electrons and holes introduced at suitable electrodes approach each other, being able to form excimer, exciplex and molecular emissive states. However, by definition, they have to pass an intermediate stage of coulombically-correlated electron–hole pairs. Radiative 'cross transitions' between closely spaced, but different, molecules may then be observed, modifying the effective EL emission spectrum. Such "prepared" emissive electron –hole pairs have been named *electromers* and *electroplexes*, respectively [2].

In the present paper, the emission features of B-M excited states will be identified and demonstrated in all luminescence phenomena with particular attention to those occurring in organic light emitting devices (LEDs).

2. Types of excitons

A collision of a photon with an electrically neutral atom or a molecule can transfer an electron from it to another site situated at various distances. Depending on the strength of the inter-atom (inter-molecular) interactions, the electrons and holes created in this way become either free carriers (we observe the intrinsic photoconductivity) or become coupled charge pairs called *excitons*. As shown in Fig. 1, these are large-radius Mott–Wannier excitons, small-radius (Frenkel or molecular) excitons and intermediate (one or two-molecular distances in size) charge-transfer excitons. While large-radius excitons are formed in tightly-bonded inorganic semiconductors, the latter two are characteristic of weakly-bonded organic solids. Also, it is worthy to note that Mott–Wannier excitons, being weakly-bonded, and therefore easily dissociating, are usually observed at low temperature. For organic solids, the emission, as a rule, originates from excitons, even at room temperature, as band-to-band transitions are very inefficient in them.

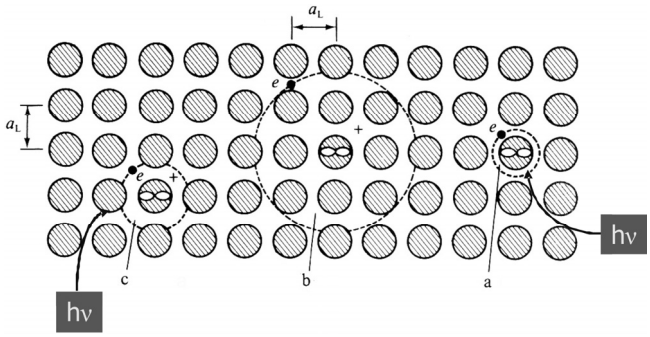


Fig. 1. General classification of excitons in solids: a) localized excited state: Frenkel or small radius exciton, b) Mott–Wannier or large radius exciton, c) charge pair (one or two intermolecular distances) intermediate size exciton. Excitation by a photon is indicated as *hν*. For explanations see text

3. Excimers and electromers in PL and EL

In single-component organic solids composed of chemically identical molecules which do not aggregate in their ground states (do not form dimers or larger aggregates), the formation of B-M excited states is possible, due to resonance interactions of a molecular exciton with neighbour non-excited molecules. They are called 'excimers' [2, 4] or 'electromers' [2, 6, 7]. Exciton and charge-transfer resonance can be defined by intermolecular exchange of the singlet or triplet excitation energy and/or charge. The first process leads to the so called 'locally-excited excimers' (local excimers), the second to 'charge-transfer excimers' (CT excimers). In general, mixed excimers are formed and described by local ('loc') and 'CT' eigenfunctions of the Hamiltonian pair , with different amplitudes c_1 and c_2 (see Fig. 2).

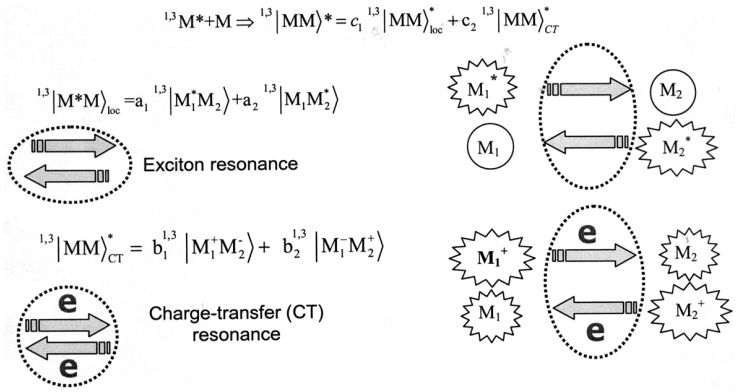


Fig. 2. Quantum mechanical description of the excimer state (either singlet,1, or triplet, 3) composed of a locally excited (loc) and charge-transfer (CT) components of this B–M excited state formed in the exciton and CT resonance interactions as illustrated by block arrows coupling two molecules

The eigenvalues of the Hamiltonian determine the energy of excimer:

$$^{1,3}E_{(MM^*)} = \left(\left[{}^{1,3}E_{M^*} \mp \frac{\mu^2}{r^3}(\cos\alpha - 3\cos^2\theta) \right] \mp E_{M^+M^-} \right) \tag{1}$$

It is a function of the energy of the molecular exciton ($^{1,3}E_{M*}$) and isotropic Coulombic interaction energy ($E_{M^+M^-}$). Equation (1) shows the interaction energy dependence on the intermolecular distance (r) and the mutual orientation of the interacting molecules given by two angles defined by the directions between their transition moments (μ), as shown in Fig. 3.

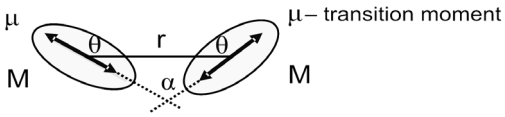


Fig. 3. The parameters determining the excimer energy (see Eq. (1))

Of the two energy levels, usually the lower one is responsible for the radiative transitions. In Figure 4, the lack of dimers in the ground state molecules is apparent, through the monotonically decreasing repulsive potential, and a shallow minimum on the potential curve of the excimer.

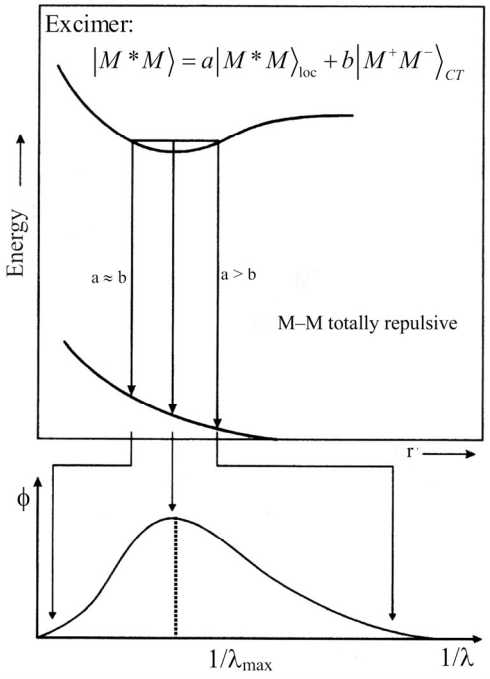


Fig. 4. Excimer energetics: potential energy diagram (upper part), and emission spectrum (bottom part). For discussion see the text

We note that the shape of the emission spectrum depends on the composition of the mixed excimer. Lower energy transitions correspond to a substantial contribution of the CT excimer ($a \approx b$), and higher energy transitions correspond to a larger contribution of the loc excimer. From quantum mechanical calculations, it follows that no pure loc and CT excimers can exist. Moreover, at distances exceeding 0.4 nm they lose their excimer features, dissociating into isolated molecular species or possibly electron–hole pairs still bound by the Coulombic attraction. In a typical aromatic excimer, the equilibrium distance r_0 amounts to about 0.33 nm.

The effect of intermolecular conformation on the emission spectrum is well illustrated by anthracene excimers, as shown in Fig. 5.

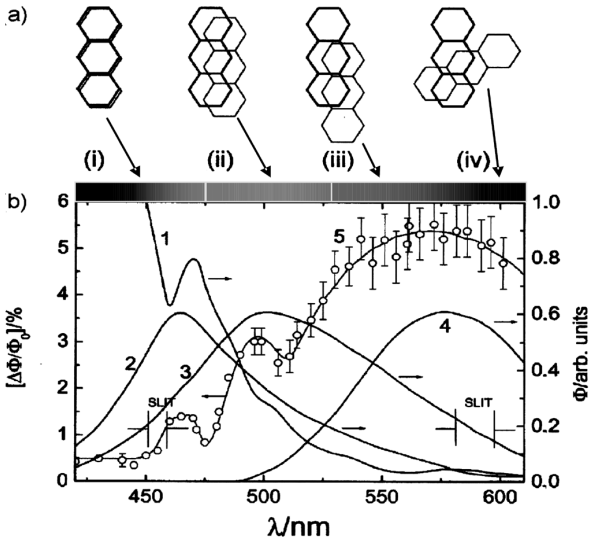


Fig. 5. Various excimer conformation PL spectra in solid anthracene, curves 1–4 [8–10]. The action spectrum of the PL quenching by injected holes in an anthracene single crystal is shown for comparison (points) [11]. For discussion see text

An incipient dimer formed by exact parallel overlapping of two molecules in anthracene single crystal: (1) gives an emission that is almost the same as the emission of slightly "slided" molecules; (2) from low-temperature evaporated films, both suggesting a large contribution from the "loc" excimer component, broad-band (3) originates from a molecular pair with molecules displaced by one benzene ring, and (4) two molecules turned around an axis perpendicular to their planes, as formed in the photocleavage of single di-anthracene crystal. The latter suggests the CT excimer to be dominating. Interestingly, all of these conformation emissions are reflected in photo-luminescence quenching by injected holes (points).

Electromers are defined by a separated, but coulombically-correlated, electron –hole pairs which can decay with a non-zero cross transition radiative rate constant. Therefore, their formation requires the intermolecular charge separation when excited

optically, or independent sources of holes and electrons that undergo bimolecular recombination in a luminescent material [6].

3.1. Generation by electron–hole recombination

Free electrons (e) and holes (h), introduced, e.g., at suitable electrodes, approach each other being able to form either excimer or molecular emissive states (Fig. 6). They, by definition, have to pass an intermediate stage of Coulombically-correlated electron–hole pairs (e…h). Due to spin statistics, three times more triplet ^{3}(e…h) than singlet ^{1}(e…h) pairs are created, that is their creation probabilities amount to P_T=3/4 and P_S = 1/4 , respectively.

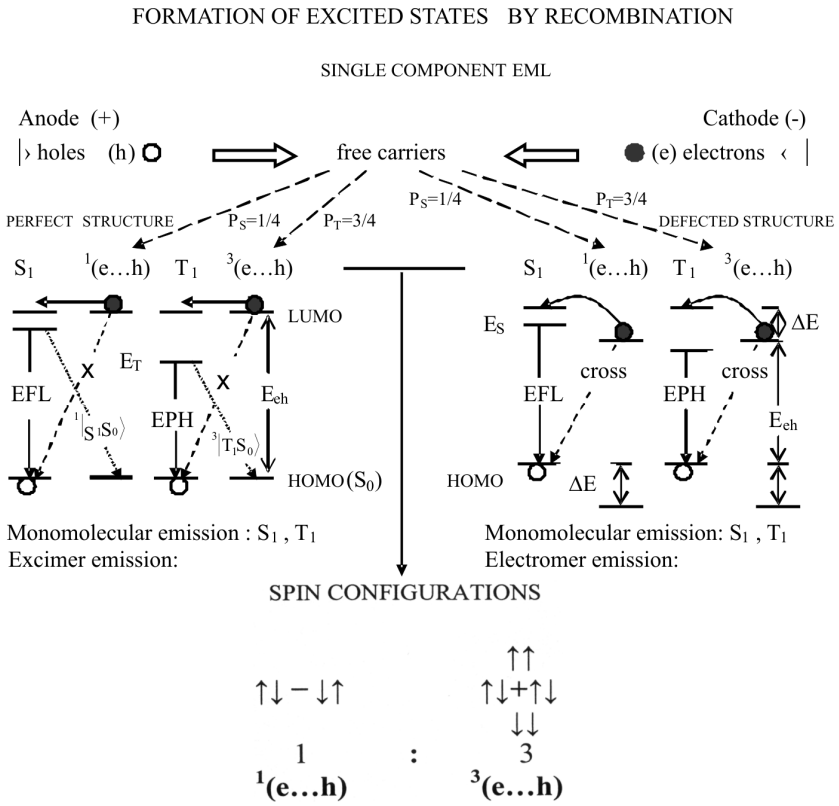


Fig. 6. Generation of excited states by electron–hole recombination in single-component emitters. The effect of defects on the recombination products is shown in the right-hand part of the figure (adapted from [12]). For explanations see text

Another important point is the structural quality of the luminescent material. In a perfect structure, the LUMOs (Lowest Unoccupied Molecular Orbitals) and HOMOs (Highest Occupied Molecular Orbitals) of all molecules are on the same level, the

charge motion is due to hopping over a barrier dependent only on the molecular structure and the intermolecular distance. Radiative electron–hole "cross transitions" between neighbour molecules are highly ineffective in competition with charge recombination on one molecule (it is indicated by bold crosses in the left-hand side of Fig. 6). Thus, the emission originates from molecular excitons (electrofluorescence or electrophosphorescence) and possibly from singlet and triplet excimers. In disordered structures with defects, the hopping time becomes much longer because, there, an additional barrier (ΔE) for charge hopping can appear due to local defects. Radiative cross transition may become detectable in the long-wavelength wing of the emission. Such "prepared" emissive electron–hole pairs have been named *electromers*. They can be observed in simple molecules of anthracene and in more complex molecules. Figure 7 compares PL and EL spectra from a 20% anthracene:polycarbonate blend.

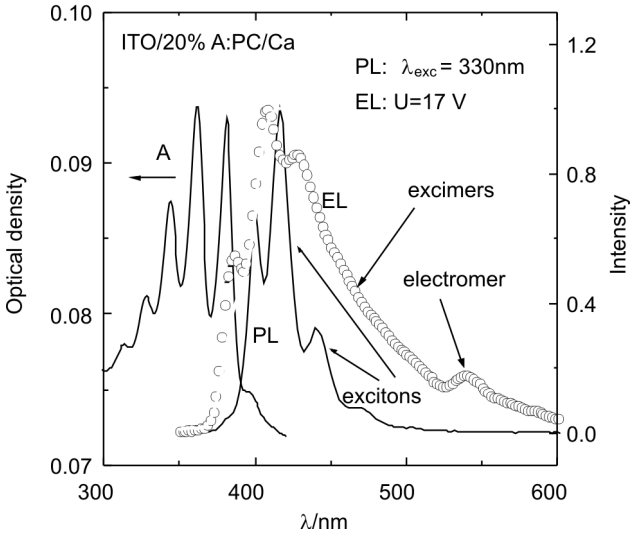
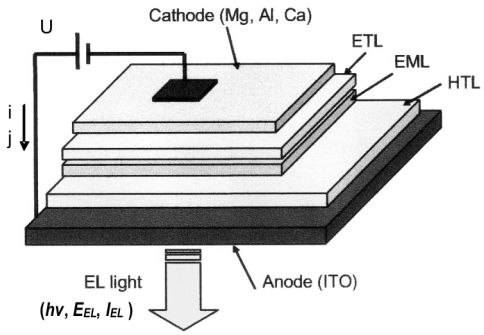


Fig. 7. Comparison of PL and EL from a 20% anthracene–polycarbonate blend emitter. EL originates from a single-layer LED with ITO and Ca provided anode and cathode, respectively. We note the differences between PL and EL spectra, caused by the apparent presence of B-M states (excimers and electromers) in the EL spectrum [7]

In PL, molecular emission is apparent with well-resolved, vibrational progression. In EL, a combination of emission from various types of excimers forms a long-wavelength tail of the emission spectrum. In addition, a well-resolved bump at about 530 nm can be seen. This feature has been ascribed to an electromer [7].

3.2. Excimer LEDs

Recall the idea of a simple, double-layer organic LED (Fig. 8). What is an organic light emitting device?

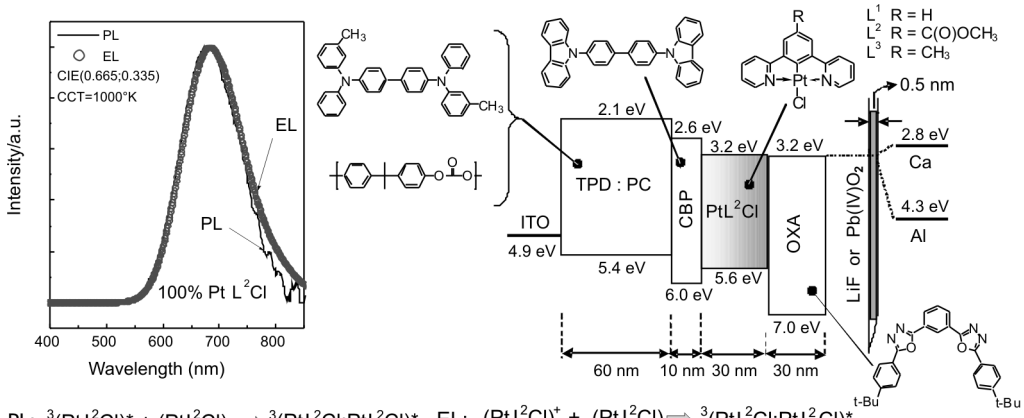


$$\eta = \frac{E_{EL}}{Ui}$$

$$\phi_{EL} = \frac{I_{EL}/h\nu}{j/e} = \frac{eU}{\langle h\nu \rangle}\eta \quad \frac{\text{photons}}{\text{electron}}$$

Fig. 8. Fundamental setup of a double layer (DL) organic LED: ETL– electron transport layer, EML – emission layer (20–100 nm), HTL – hole transport layer. Indium–tin oxide (ITO) covered glass (or quartz) substrate is used typically as a hole-injecting contact and a metal (usually Mg, Al, Ca) as an electron injecting electrode. Adapted from Ref. [12]

It consists of a system of thin organic layers provided with a transparent semiconductor hole-injecting anode (usually indium–tin oxide, ITO) and a metal electron-injecting cathode. Electron- and hole-transporting layers are marked by ETL and HTL, respectively. LED performance is characterized by the power conversion efficiency (η) and the quantum electroluminescence efficiency (φ_{EL}); the latter is defined as the ratio of the light quantal flux ($E_{EL}/h\nu$) and the electron stream (j/e) driving the device. The heart of an organic LED is its emitter layer (EML), containing a fluorescent or phosphorescent material. Depending on its emission spectrum, colour LEDs or white LEDs can be fabricated. In an EML, excimers can be formed and their emission observed through the transparent ITO anode.



PL: $^3(Pt\,L^2Cl)^* + (Pt\,L^2Cl) \Rightarrow {}^3(Pt\,L^2Cl{:}Pt\,L^2Cl)^*$ EL: $(Pt\,L^2Cl)^+ + (Pt\,L^2Cl) \Rightarrow {}^3(Pt\,L^2Cl{:}Pt\,L^2Cl)^*$

$$^3|MM\rangle^* = c_1{}^3|MM\rangle^*_{loc} + c_2{}^3|MM\rangle^*_{CT} \quad (c_2 >> c_1)$$

Fig. 9. Read/near-infrared excimer LEDs using Pt complexes with various substituents L^n (here a PtL^2Cl-based LED is demonstrated). Two different ways of the formation of excimer triplets in PL and EL are pointed out. The Commision Internationale de L'Eclairage (CIE) and Correlated Colour Temperature (CCT) of the emission are shown aside the PL and EL spectra. Adapted from Ref. [13]

An interesting class of excimer-forming molecules are flat platinum complex molecules. An example of such highly phosphorescent molecules (PtL^nCl) is shown in Fig. 9. Its neat film PL and EL spectra coincide, peaking at about 700 nm, and suggesting CT excimers dominating the emission. We note that the heavy Pt atom enhances the singlet-triplet intersystem crossing rate constant, thus leading to the formation of triplet excimers. As shown in Fig. 9, such films can form an emission layer in a four-layer LED; layers of CBP and OXA confine the recombination and emission to the emitter layer, due to their blocking function for particular charge carriers and triplet excitons. Changing the ligand allows the spectrum to be red shifted as illustrated in Fig. 10a.

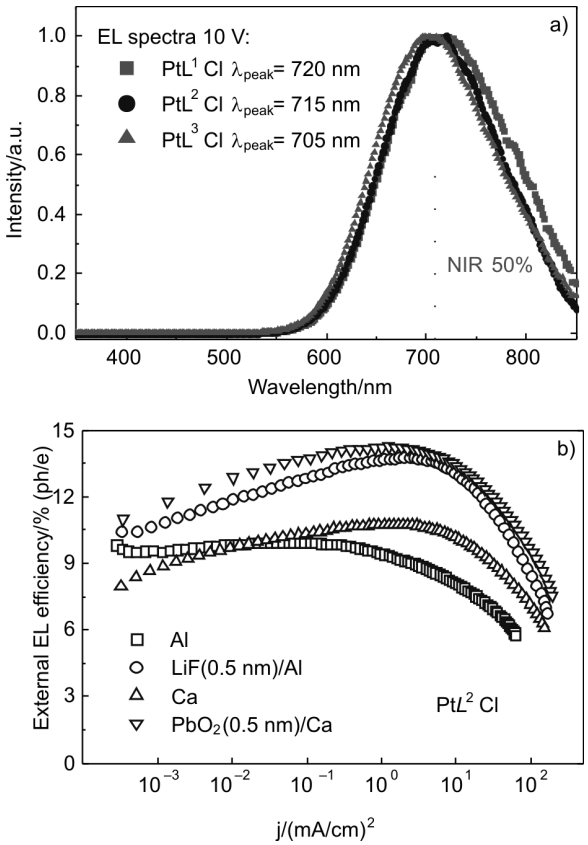


Fig. 10. EL emission spectra from neat films of PtL^{n}Cl with various ligands (a) [14] as indicated in Fig. 9, and EL external quantum efficiency as a function of driving current of a LED (b) based on a neat film emitter of PtL^2Cl with different buffers at the cathode [13]. The LED architecture as given in Fig. 9

The emission maximum for a hydrogen atom as a ligand is located at about 720 nm, the NIR region, above 700 nm, covers roughly 50% of the whole spectrum, with still high quantum efficiency. These LEDs exhibit so far the highest quantum efficiencies in the NIR region, exceeding 9% ph/e for all buffer layers in front of the cathode, and reaching almost 15% ph/e for a lead (Pb) oxide buffer (Fig. 10b).

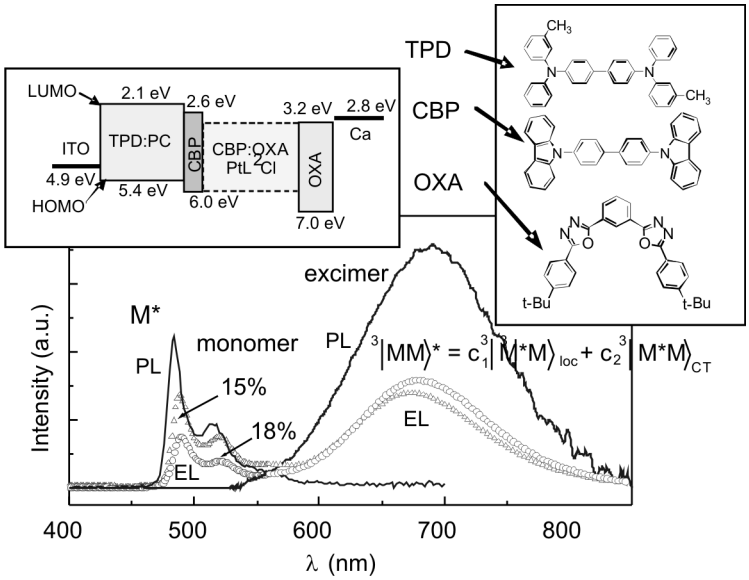


Fig. 11. EL emission spectra of PtL^2Cl-doped blend emitters (15 and 18 wt. %) from a four-layer LED depicted in the left upper inset compared with the PL spectra of a 5 wt. % -doped blend (monomer emission) and a 100% neat PtL^2Cl film (excimer emission). The molecular structures of some component materials used are given in the right-upper inset. Adapted from Ref. [15]

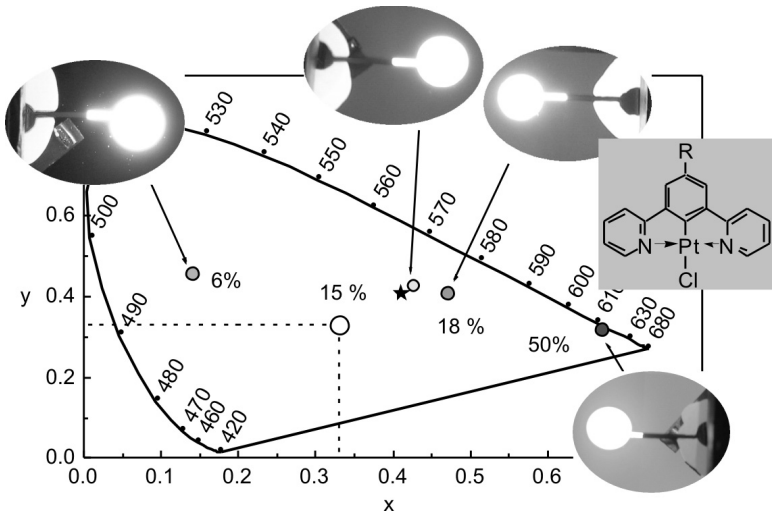


Fig. 12. Colour and white LEDs by manipulating the concentration of the complex concentration in blend emitters. Here, 6, 15, 18 and 50 wt. % of PtL^2Cl blended with a CBP:OXA emitter, all in the LED's architecture shown in Fig. 11. Taken from Ref. [15]

It must be pointed out that the emission spectrum of a low concentration (below 5 wt. %) complex solid solution displays a well-structured phosphorescence spectrum, as compared with a broad, structureless excimer spectrum peaking for L^2 ligand at

about 660 nm. From the data of Fig. 11, two emission bands (molecular triplet and excimer) are observed for 15% and 18% concentrations of the Pt complex in a blend with CBP and OXA. By adjusting the concentration, the monomer-to-excimer band ratio can be changed and the LED colour change follows (Fig. 12).

At a low concentration complex level, a blue emitting diode dominated by the monomer emission can be fabricated, a red shift is observed as the concentration increases from 15% up to 50%, an increase of the excimer emission largely dominates at high concentrations. For a certain concentration (here about 15 wt. %) the CIE chromaticity coordinates fall close to those characteristic of soft white light (star) from incandescent light sources. This provides a simple way to prepare white light emitting diodes.

3.3. Exciplex LEDs

In two-component blends composed of an electron donor (D) and an electron acceptor (A), the formation of bimolecular excited states by electron transfer from donor to acceptor molecules is highly facilitated. In analogy to single-component systems they are called *exciplexes* and *electroplexes* (see Fig. 13). An example is shown in Fig. 14.

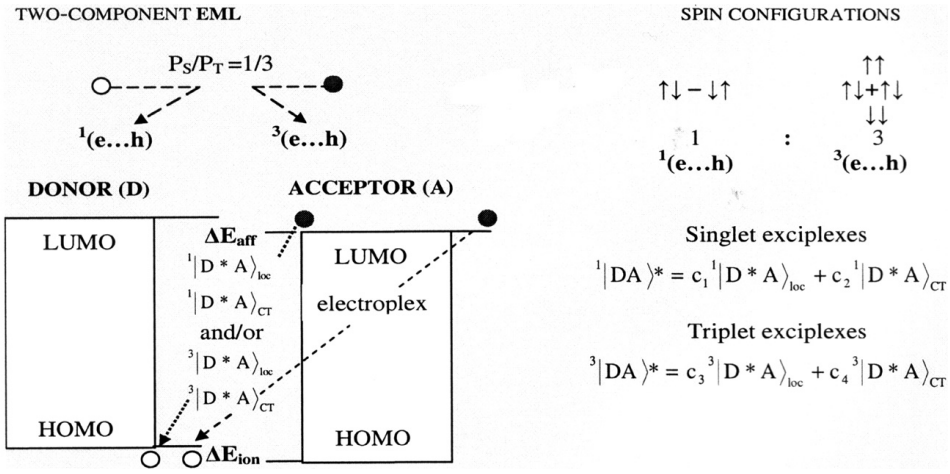


Fig. 13. The formation of bimolecular excited species (exciplex and electroplex) in two-component (electron donor (D) : electron acceptor (A)) organic solids [12]

Relatively narrow and structured spectra of individual donor (TPD) and acceptor (PBD) molecules switch to broader, structureless PL and EL spectra for their blends. In addition, a distinct difference between PL and EL spectra is apparent. The PL spectrum ascribed to the exciplex emission becomes more complex under electrical excitation. The EL spectrum at the photon energy scale can be decomposed into Gaussian profiles showing 4 different emissive species.

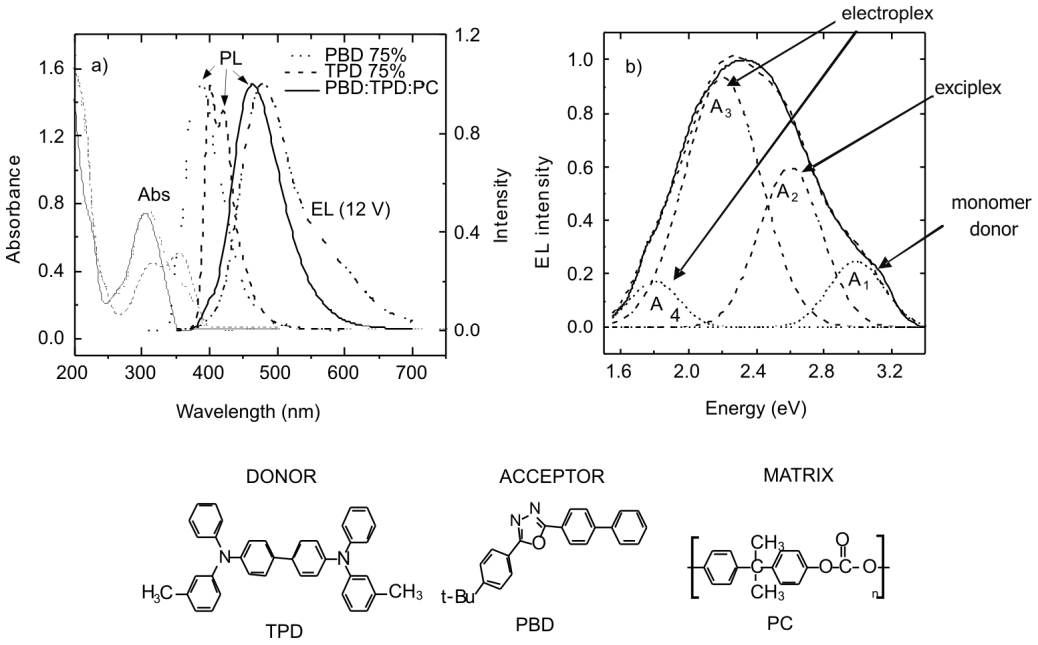


Fig. 14. (a) Emission spectra from an electron donor (TPD), electron acceptor (PBD) (PL) and from their blend in a neutral binder (PC), TPD:PBD:PC (PL and EL). (b) Photon energy representation of the broad EL spectrum of the blend from part (a). Its decomposition into Gaussian components shows the spectrum to be a combination of the emission from different types of the excited monomer and B-M states: monomer, exciplex and electroplex indicated respectively in the figure [16]

Besides of the maxima A_1 associated with monomer emission of the donor (D) and A_2 associated with the exciplex emission in both PL and EL spectra, two additional long-wavelength bands can be distinguished in the EL spectrum assigned to two different electroplexes due to cross transitions between two molecules with slightly different distances (one or two intermolecular spacings).

Like excimers, exciplexes can be formed as a result of both exciton and charge transfer resonances, a mixed type exciplex is composed of local (loc) and CT exciplexes (Fig. 15).

The emission maximum is determined here by a simple relation between the ionization potential of the donor (I_D), the electron–hole Coulombic attraction energy (E_C), and the electron affinity of the acceptor (A_A) (which is stabilized by E_C),

$$h\nu_{EX}^{\max} \approx I_D - A_A - E_C \tag{2}$$

$$E_c = \frac{e^2}{4\pi\varepsilon_0\varepsilon r} \tag{3}$$

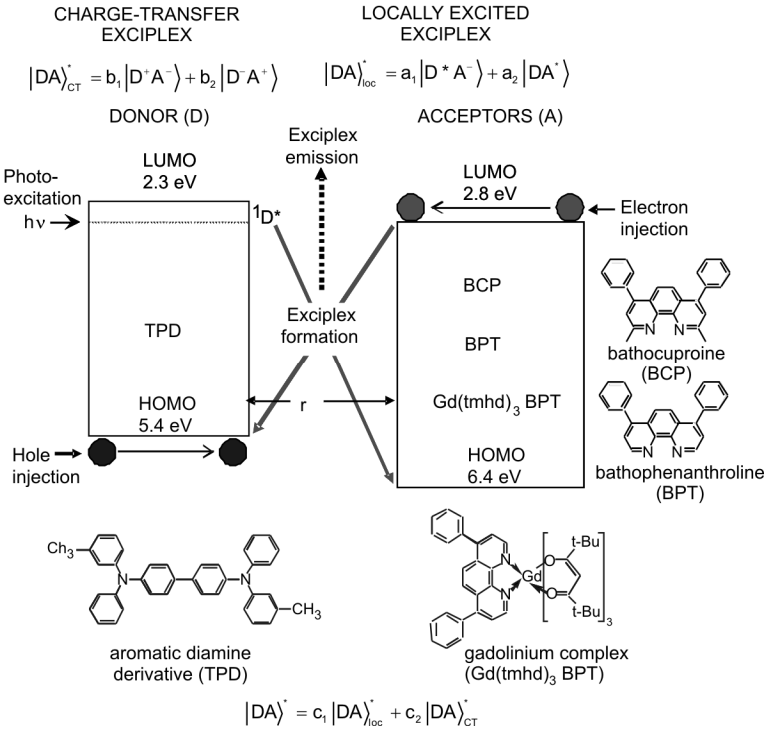


Fig. 15. Exciplex types and their formation mechanisms under optical ($h\nu$) and electrical ($e + h$) excitation for an electron donor (TPD) and three various acceptors (BCP, BPT, $Gd(tmhd)_3BPT$). In general, the exciplexes are composed of a 'loc' and 'CT' components and can have either singlet or triplet character dependent on the acceptor (cf. Fig. 16)

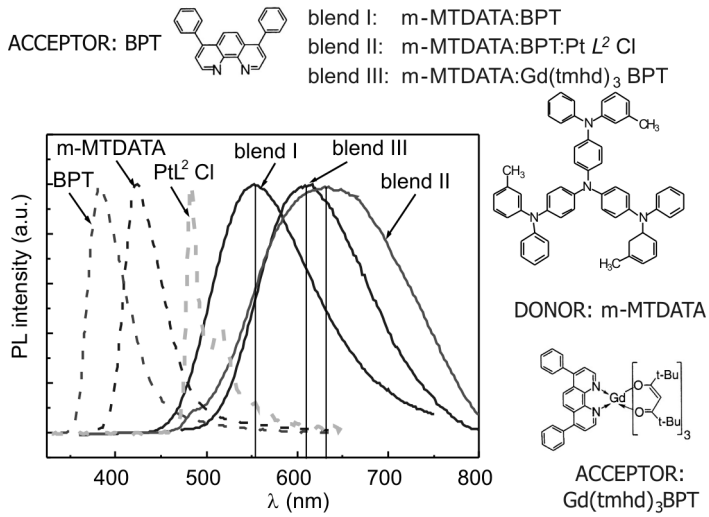


Fig. 16. PL spectra of exciplex emitter films with an electron donor m-MTDATA and two various acceptors BPT and $Gd(tmhd)_3BPT$ incorporated in a PC binder. Adapted from Ref. [17]

Like in the case of excimers, stable exciplexes can be formed at distances below 0.4 nm. An interesting observation comes out from the exciplex spectra associated with various acceptors (Fig. 16). Again, we can see relatively narrow molecular emission spectra of individual components of various donor–acceptor blends, and broad, red-shifted spectra of the latter. Interestingly, replacing an acceptor BPT with its Gd-substituted derivative, shifts the exciplex emission spectrum to the red. An explanation is that in contrast to the donor-BPT system, where singlet exciplexes are formed, the same donor Gd substituted BPT leads to triplet exciplexes. The heavy gadolinium atom enhances singlet-triplet intersystem crossing transitions, resulting in the creation of triplet exciplexes. A similar effect is observed with the Pt complex blend, where exciplexes with the Pt complex dominate, showing its triplet character. Based on these properties, efficient exciplex LED structures have been fabricated (Fig. 17).

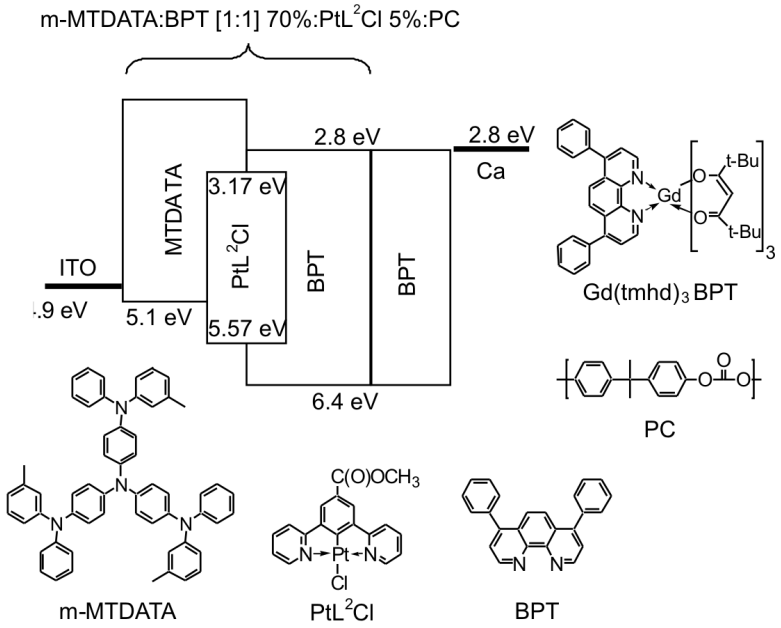


Fig. 17. An exciplex LED structure with an electron donor (m-MTDATA) and three various electron acceptors (BPT, Gd(tmhd)$_3$BPT, and PtL^2Cl) incorporated in a PC binder [18]

These are double-layer LEDs composed of the ETL of BPT and the Pt complex-doped emitter layer (also, acting as HTL) with ITO-hole injecting anode and calcium-electron injection cathode. A time resolved study of the PL and EL from such LEDs with different blends, provided a strong evidence that different spin multiplicity occurs in emissive exciplexes. Interestingly, a difference between the emission spectra from blend I and blend III is clearly apparent, suggesting the first one to be underlain by singlet and the second to be underlain by triplet exciplexes. Indeed, as expected, the emission decay for triplets is an order of magnitude longer than that for singlets (Fig. 18).

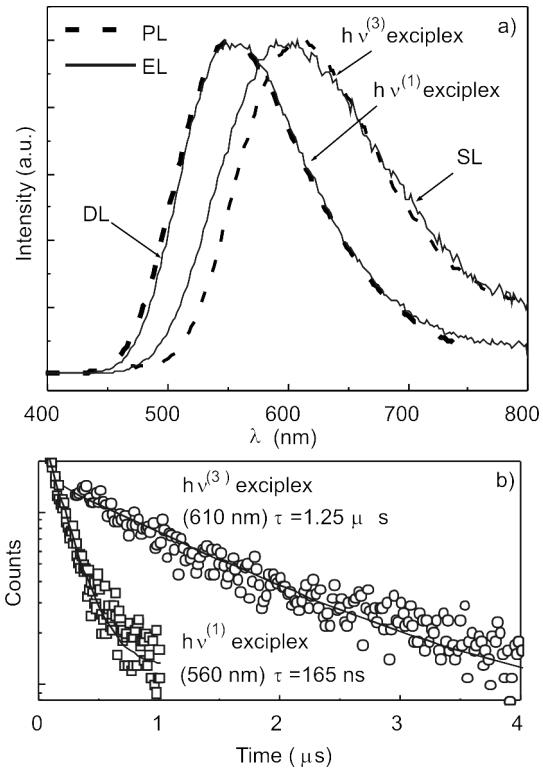


Fig. 18. Emission (PL and EL) spectra of the exciplex LED structures (a) depicted in Fig. 17. $h\nu^{(1)}$: blend I, m-MTDATA:BPT; $h\nu^{(3)}$: blend II, m-MTDATA:BPT:PtL^2Cl and blend III, m-MTDATA:Gd(tmhd)$_3$BPT. The EL spectrum of a single-layer (SL) LED (ITO/m-MTDATA:BPT:PC/Ca) is shown for comparison; PL decay curves (b) at the maxima of the fluorescence (560 nm) and phosphorescence (610 nm) exciplex spectra excited at 336 nm under argon atmosphere. The decay time for $h\nu^{(3)}$ decreases by about 30% in the ambient air (not shown in the figure)

Now, let us recall our earlier conclusion that bimolecular excited states in PL and EL occur in opposite ways. While in PL a molecular excited state interacts with a ground state molecule, leading to a partial transfer of charge, in EL the primary stage is due to separated carriers. One of the consequences is that much more triplet states are formed under charge carrier recombination conditions. We should expect more triplet exciplexes to be formed, dominating triplet exciplex emission. In fact, in a TPD donor–BCP acceptor system two exciplex bands are observed in EL (Fig. 19): band G_1 belongs to singlet exciplexes, and band G_3 belongs to triplet exciplexes.

Only the G_1 band appears in the PL spectrum proving efficient formation of primary singlet excitons. The ratio of G_1-to-G_3 band emissions depends on the electric field. Using a gadolinium substituted complex as an acceptor makes the PL and EL spectra quasiidentical. In both cases, the production of molecular triplets dominates the primary generation process. A slight shift between PL and EL spectra for this sys-

tem may be attributed to a difference in amplitudes of loc and CT components of the mixed excimer, the CT component, understandably, contributing more in EL emission.

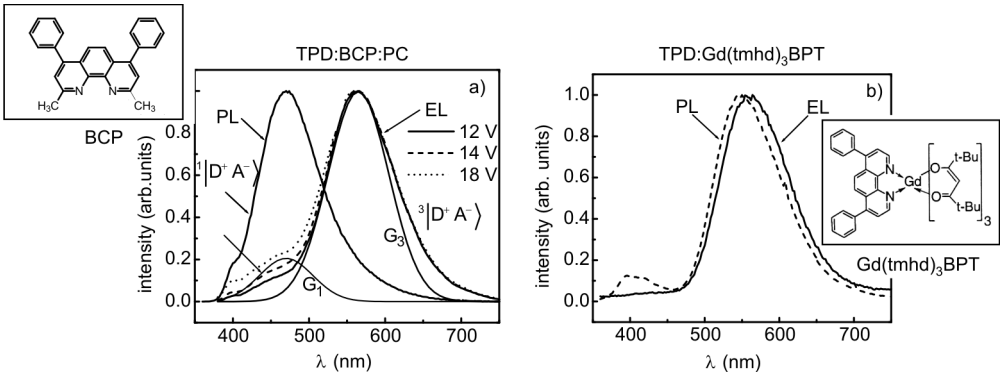


Fig. 19. PL versus EL exciplex spectra for an electron donor TPD and two electron acceptors BCP (a) and Gd(tmhd)$_3$BPT (b). While the singlet exciplex underlain PL spectrum and singlet-triplet mixture underlain EL spectrum (bands G_1 and G_3, respectively) for the BCP acceptor are observed, solely triplet exciplex underlain PL and EL emissions are revealed for the Gd(tmhd)$_3$BPT acceptor [19]

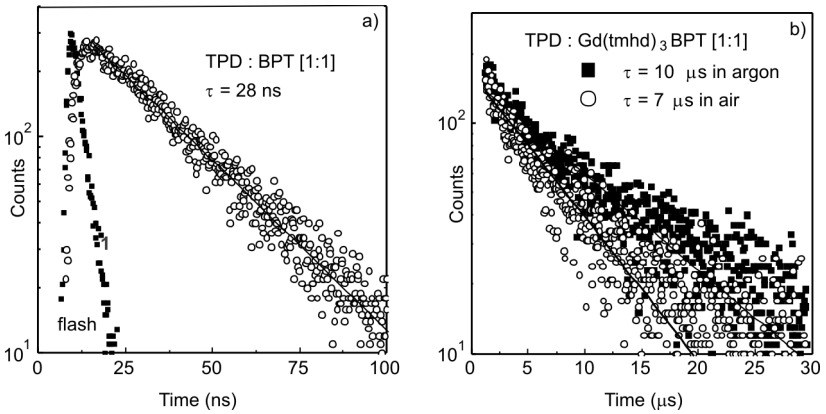


Fig. 20. Triplet versus singlet exciplexes: PL decays for G_1 (a) and G_3 (b) emission bands from Fig. 18. While the G_1 band emission decay on the nanosecond scale is typical of singlet exciplex states, the G_3 band emission decay on the microsecond scale indicates its triplet character. The latter is strongly supported by a shortening of the lifetime when the sample is placed in ambient air [19]

Is there any other proof of the triplet character of the band G_3? The answer is yes. In Figure 20, we see photoluminescence decay profiles for bands G_1 and G_3. Clearly, the short time decay at band G_1 (ten nanosecond scale), independent of the ambient atmosphere, contradicts the much longer time for band G_3 (ten microsecond scale in argon), being reduced by about 30% in air, where triplet are quenched by oxygen.

Recently, we have shown [20] how white light emitting diodes can be improved, combining monomer, excimer and exciplex emissions all together within a single dopant emitter (Fig. 21).

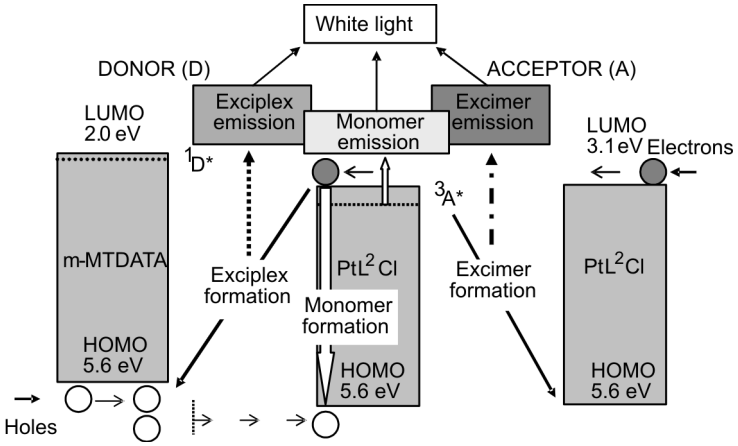


Fig. 21. Combining monomer, excimer and exciplex emissions a way to improve performance of white LEDs [20]. Copyright Wiley, VCH Verlag GmBH & Co. KGaA. Reproduced with permission

As a dopant we have chosen a phosphorescent Pt complex, also playing the role of the acceptor incorporated in a donor matrix of TPD or m-MTDATA. In this system, the Pt complex dopant can emit monomolecular phosphorescence, excimer phosphporescence and exciplex phosphorescence, the latter emanating from triplet exciplexes formed from donor–dopant interaction (Fig. 22).

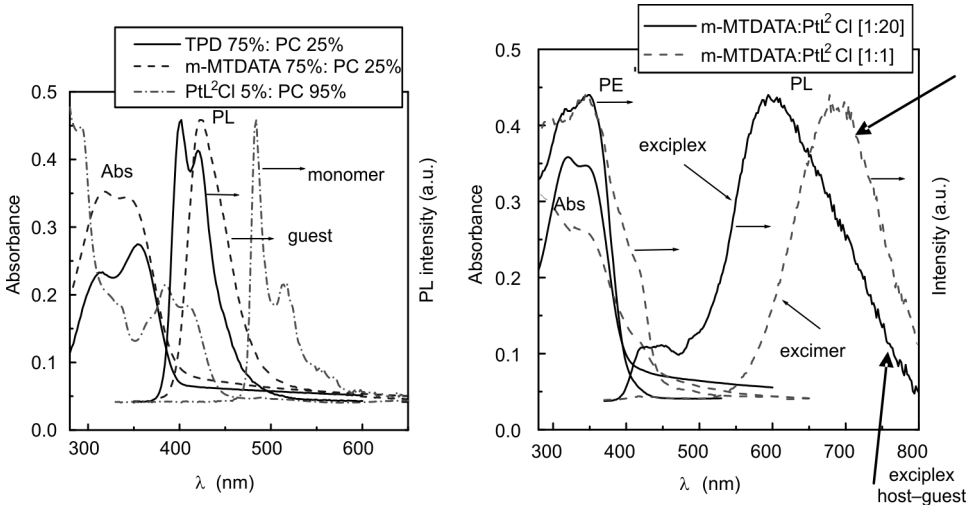
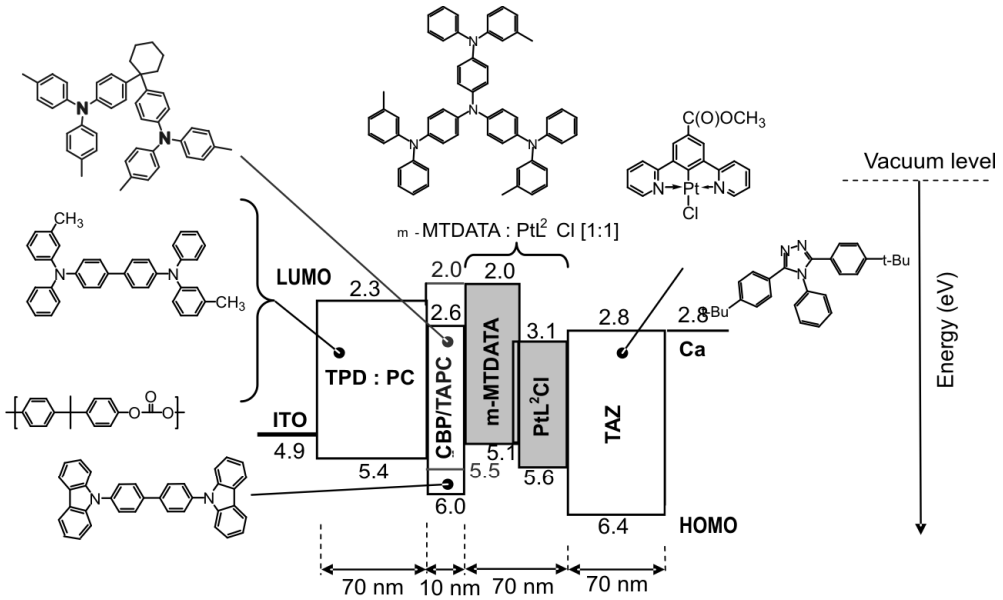


Fig. 22. PL spectra of TPD, m-MTDATA and PtL^2Cl, and their blends in PC, along with their absorption and photoexcitation (PE) spectra [20]. Molecular structures of the materials used are given in Fig. 23

An efficient white light emitting diode with a particular colour rendering index (CRI) has been fabricated [20]. Its architecture, along with the values of its most important performance parameters, is given in Fig. 23.



Selected performance characteristics of organic MEE LED

Structure	φ_{ext} [% ph/e]	η_P [lm/W] (L) [cd/m^2]	CIE*	CRI**
MEE LED	6.5	9.0 (500)	(0.46, 0.45)	90

*CIE – Commission Internationale de l'Eclairage; ideal white light CIE coordinates are (x=0.33, y=0.33) and those for warm incandescent lamp light are (0.41, 041).
** CRI – colour rendering index; for ideal white light CRI=100.

Fig. 23. Monomer : excimer : exciplex (MEE) white LED. Selected performance parameters are given below its schematic architecture [20]

It is a 4-layer LED of total thickness 220 nm, provided with an ITO hole injecting anode and an electron injecting calcium cathode. Its CIE coordinates are close to warm, incandescent lamp light (0.41, 0.41) and its CRI is as high as 90, as compared with the index of 100 for ideal, white light.

4. Exciplexes in electrophotoluminescence (EL-PL)

Electrophotoluminescence (EL-PL) comes into existence when optically excited film is subjected to injection of electrons and holes from suitable electrodes (Fig. 24). In Figure, 25 we see such a system with a hole injecting ITO and electron injecting calcium applied to exciplex emitting films of an electron donor (m-MTDATA) and an

electron acceptor of the Pt complex Pt L^2Cl, which has already been discussed. The total emission consists of PL and EL components. The electric field effect on the emission signal is shown in Fig. 26.

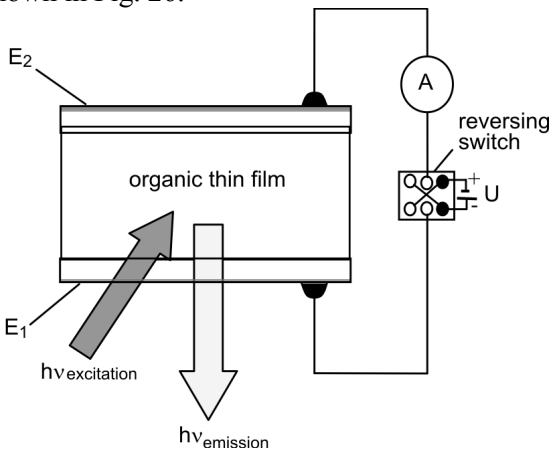


Fig. 24. How electrophotoluminescence comes into existence

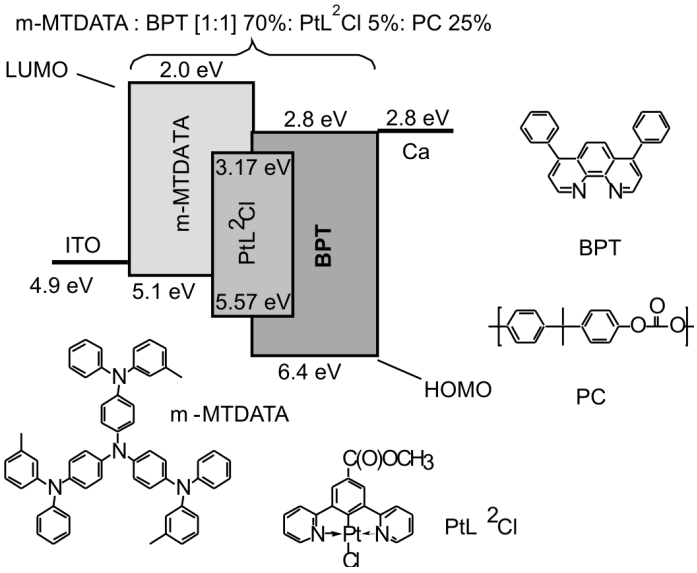


Fig. 25. The energy level scheme of materials forming the blend emitter of a single-layer (SL) LED with ITO and Ca injecting anode and cathode, respectively. After Ref. [5]

With the electrical polarization blocking charge injection (ITO^-), the PL signal is reduced, we observe only the quenching effect (δ-positive). For the forward polarization, the low-field quenching is followed by a signal increase (δ-negative quenching). Under a certain electric field, a reduction in the emission is compensated by the enhancement, the quenching of total emission diminishes to zero, no electric field effect

on the total emission is visible. It is understandable that the zero field effect is a function of the light excitation level, injection efficiency of electrodes and the phosphorescence efficiency of the exciplex [5].

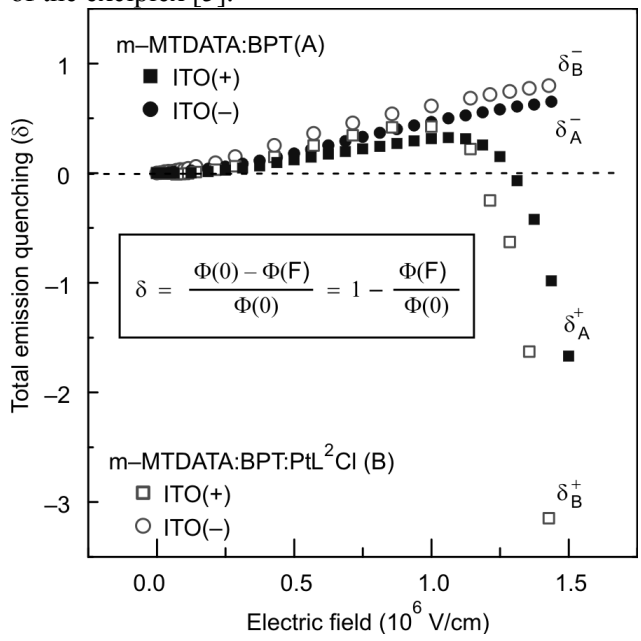


Fig. 26. Electric field effect on the total effective emission quenching (δ) defined by a relative change in the emission light flux (EL-PL) in the absence ($\Phi(0)$) and presence ($\Phi(F)$) of electric field (F) applied for two SL LEDs designated in the figure as devices (A) and (B). We note the effect to be positive ($\delta > 0$) reflecting the real quenching (a reduction in the light flux), negative quenching ($\delta < 0$) reflecting and enhancement of the light flux, and $\delta = 0$ for a certain electric field (reversing field) that is no change in the light flux at this field value [5]

A straightforward application of this phenomenon is mutual control of electrical and optical signals in various optoelectronic devices. For non-injecting electrodes (reversed bias), the considered film structures already function as luminescence attenuator devices. Charge injection (forward bias) into these films makes it possible to exploit them in devices that, upon voltage switching, can be changed from luminescence attenuators to luminescence amplifiers.

5. Concluding remarks

Bimolecular excited states, like excimers and exciplexes, can be efficiently produced in organic solids, especially under electrical excitation (recombination electroluminescence). These states essentially modify their electronic properties. This opens up the unusual possibility to tailor the performance parameters of organic optoelectronic devices.

We have seen numerous examples of organic light emitting diodes (LEDs): (i) organic material blends can be prepared to form thin film emitters for colour, white and near IR efficient LEDs; (ii) very high external quantum efficiency > 16% ph/e and > 10% ph/e have been achieved for white LEDs (WLEDs) and NIR LEDs, respectively, based on the diversity of excited states. Further improvements of WLEDs are expected, employing a combination of emissions from monomers, excimers and exciplexes formed by electron acceptor emitters and electron donor binder matrices. Further improvements of IR LEDs can be achieved by the application of more efficient electron injecting electrodes.

Bimolecular excited states enable mutual control of optically and electrically excited luminescence signals (EL-PL) in a way that allows for the manufacture of optoelectronic switches (electrical field switching from luminescence enhancing to luminescence attenuating devices).

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