

CURRENT TRENDS IN ORGANIC LIGHT-EMITTING DIODES

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ABSTRACT

In recent years, organic light emitting diode (OLED) technology is rapidly growing in commercial market place for a wide range of product applications: from today's small area mobile display products to tomorrow's large area televisions and eventual general lighting applications. Today, the displays based on OLEDs have become commercially available. After 1987, great developments have taken place in enhancing the efficiency and increasing the stability of OLEDs emitting different colours of light. On the basis of the processes and materials used there are three generations of OLEDs, namely, fluorescent, phosphorescent and thermally activated delayed fluorescent OLEDs. The present paper reports the recent advances in OLEDs and discusses the salient features of three generations of organic light-emitting diodes. In fluorescent OLEDs the maximum internal quantum efficiency is 25% because only the singlet excitons emit light. The use of phosphorescent heavy metal-organic complexes as dopant in fluorescent materials exploits the normally non-radiative triplet excitons and so enhances the overall internal quantum efficiency to 100 %. Recently, a new class of metal-free organic electroluminescent molecules have been reported, in which the molecules harness both singlet and triplet excitons for light emission through fluorescence decay channels and provides an intrinsic fluorescence efficiency in excess of 90 % and a very high external electroluminescence efficiency of more than 19 %, which is comparable to that achieved in high-efficiency phosphorescence-based OLEDs. Thus, great advances have been made in the development of materials for efficient and stable OLEDs, which may enhance the development related to the fabrication of new displays and solid state lighting devices.

KEYWORDS: OLEDs, OLED generations, Fluorescence, Phosphorescence.

1. INTRODUCTION

Organic light emitting diode (OLED) is a thin-film optoelectronic device, in which a single layer, double layer or multilayer of organic materials is sandwiched between two electrodes, at least one of which is transparent or semi-transparent for the transmission of light. The reports of low voltage electroluminescence from thin organic films made of small molecular weight molecules by (Tang et al., 1987) and on conducting polymers by (Burroughes et al., 1990) have opened a new field of research in organic light-emitting diodes. In recent years, OLED technology is rapidly growing in commercial marketplace for a wide range of product applications: from today's small area mobile display products to tomorrow's large area televisions and eventual general lighting applications. The OLEDs consisting of hole-and electron – transporting molecular materials or of spin – coated thin polymers films have been fabricated with active device thickness of less than one hundred nanometer. For an applied voltage of about 3 to 5V, the OLEDs emit light brighter than conventional TV screen with much higher efficiencies, brilliant colours, large viewing angle, switching times fast enough for video real time image displays and lifetime well above 100,000 hours. After 1987 great developments have taken place in enhancing the efficiency and increasing the stability of OLEDs. On the basis of the processes and materials used there are three generations of OLEDs. The present paper reports the basic principles and salient features of the three generations of organic light-emitting diodes.

2. FIRST GENERATION OLEDs: FLUORESCENT OLEDs

2.1 Construction and working of fluorescent OLEDs

Fig. 1(a) shows the schematic diagram of a single layer OLED. In this case, homogeneous dense film of the appropriate material for emissive layer (EML) is coated on transparent conducting substrates like Indium Tin Oxide

deposited onto glass by sputtering or electron beam evaporation technique. The film thickness usually lies in the range of less than 100 nm. The second electrode is obtained by vacuum evaporation on this thin film. Generally, aluminum is used because of good stability but other materials like Mg-Ag Li-Al, etc. can also be used. For connections, external wires are attached to the electrodes by conducting carbon cement or silver paint. Several workers have fabricated ITO/PPV/Al devices where single layer of organic materials has been used. In order to assist carrier injection, many workers have used electron transporting layer (ETL) and/or hole transporting layer (HTL) in the OLEDs. Fig. 1(b) shows the configuration of double layer OLED and Fig.1(c) shows the configuration of double heterojunction (DH) multilayer OLEDs.

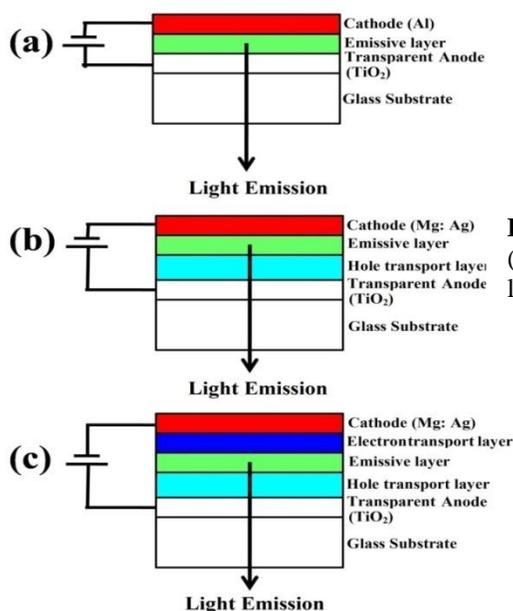


Fig.1. Configuration of (a) single layer (SL), (b) double layer (DL), and (c) triple layer (TL) OLEDs.

The principle of organic light emitting diodes is quite different from that of inorganic light emitting diodes. In OLEDs, the light emission involves the following steps (Kalinowski 2005 and Li et al, 2007): (i) injection of charge carriers from electrodes, (ii) recombination of injected charge carriers, (iii) generation of singlet and triplet excitons, and (iv) radiative decay of singlet excitons. In general, the injection of charge carriers from electrodes takes place by Richardson-Schottky thermionic emission model (at low voltage) or by Fowler-Nordheim tunneling model (at high voltage). Fig. 2 shows the energy level scheme for single layer and double heterostructure OLEDs.

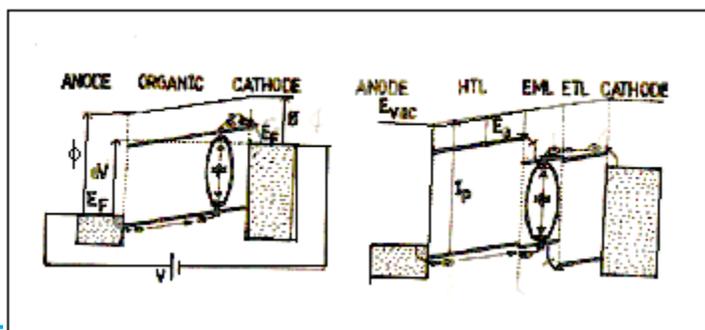


Fig. 2. Energy level scheme for single layer (left) and double heterostructure OLEDs (right) with an applied bias voltage V , illustrating the vacuum level E_{vac} , the Fermi level E_F and work function of the metallic contacts and hole and electron transport levels of the organic layers. The level offsets at the organic heterojunctions are determined by the different ionization energies I_s and electron affinities E_a of the adjacent layers.

In the single layer structure, a single component or multicomponent material is sandwiched between two metallic electrodes, which acts simultaneously as HTL, ETL and EML. In such layer, there is possibility that recombination may take place close to one of the electrodes, which may consequently decrease the EL efficiency of such structure because excited states are effectively quenched at the insulator/metal interface. However, the double layer structure composed of two different materials forming ETL and HTL allows recombination process to occur at the two insulators interface separated from the metallic contacts in which one of the materials serves as EML. Despite a considerable improvement in the EL efficiency of such double layer structure, the diffusion and quenching of excitons at one of the electrodes, especially in thin film devices, still reduces the light output. The effect can be highly limited by forming a three layer structure (a double heterostructure). The EL efficiency of such a triple layer structure increases due to the confinement of both excitons and recombining charge carriers in a thin film EML placed between different HTL and ETL materials, whereby the confinement of excitons, eliminates their quenching at the electrodes. In recent years, the OLEDs having many layers of organic materials are used, in which the efficiency and stability of OLEDs are significantly higher.

To date, the temporal, time–delay, current–voltage, brightness–current, brightness–voltage, efficiency, thermal, spectral, electrode, materials, dopant, thickness, stability, and preparation characteristics of OLEDs have been studied in detail.

2.2 Quantum efficiency of fluorescent OLEDs

Chandra et al, 2006 have derived the expression for internal quantum efficiency η_{EL} of OLEDs, which is as given below:

$$\eta_{EL} = \frac{\gamma_1}{(\gamma_1 + \gamma_2)} \cdot \frac{\delta_1}{(\delta_1 + \delta_2)} = \frac{\gamma_1}{\gamma} \cdot \frac{\delta_1}{\delta} = P_{ex} \eta_r \quad (1)$$

where γ_1 and γ_2 are the recombination coefficients for bimolecular recombination producing exciton and no exciton, respectively and $\gamma = (\gamma_1 + \gamma_2)$. δ_1 and δ_2 are the rate constants for the radiative and non-radiative decay of excitons, respectively, and $\delta = (\delta_1 + \delta_2)$. $P_{ex} = \gamma_1 / \gamma$, is the probability for the formation of excitons during the bimolecular recombination, and $\eta_r = \delta_1 / \delta$, is the efficiency for the radiative decay of excitons.

If P_s is the free –charge –carrier spin statistics, and η_{PL} is the photoluminescence quantum yield, then $n_r = P_s \eta_{PL}$. Thus, Eq. (1) can be written by as

$$\eta_{EL} = P_{ex} P_s \eta_{PL} \quad (2)$$

Because of the spin –statistics three times more triplet than singlet excited states are created in electron – hole recombination process characterized by second – order rate constants. Therefore, the probability, P_s , that a singlet excited state will be created in recombination events, is 1/4, that is, $P_s = 1/4$. For $P_{ex} = 1$ and $P_s = 1/4$, the upper limit of η_{EL} is 0.25 of the PL quantum yield. This limit can be increased up to $0.35 \eta_{PL}$, if triplet exciton annihilate to create emitting singlet.

It is evident from Eq. (2) that η_{EL} can be increased by increasing P_{ex} , P_s and η_{PL} . It has been shown that P_{ex} depends on the charge imbalance, temperature, and strength of the electric field (Chandra et al, 2006). The increase in quantum efficiency η_{EL} of OLEDs by increasing η_p , can be achieved by dopings limited amounts of fluorescent materials in the EML of fluorescent OLEDs. It has been shown previously that the quantum efficiency of OLEDs cannot exceed 25% of the PL quantum yield because only 25% singlet exciton participate in radiative process and 75% triplets excitons decay non-radiatively.

2.3 Improving quantum efficiency of fluorescent OLEDs using fluorescent dopants

In general, the quantum yield of organic materials is considerably lower in solids state. It can be increased by doping a small amount (~1 mol%) of a fluorescent dye into the conductive host materials forming EML of OLED [Tang et al 1989]. Subsequently, the increased PL yield gives rise to higher quantum efficiency of OLED. The application of electric field causes charge carrier injection and the subsequent electron- hole recombination gives rise to exciton formation in the conductive host molecules (Staudigel J. et al 1999), whereby, the excited host molecules can transfer

its exciton to the doped fluorescent molecule by a Förster mechanism (Förster energy transfer). The Förster transfer is non-radiative process and it involves the excitation of the dipole-transition of the dopant molecule by the simultaneous de-excitation of the host molecule. It requires that the excited state energy of host be equal to (i.e. resonant with) the unexcited HOMO-LUMO gap of guest molecule. For this to occur, the host fluorescence spectrum should overlap the absorption spectrum of the dopant.

There is an alternative mechanism of exciton formation on the guest molecules which requires the trapping of hole on the dopant prior to its recombination with an electron on the host (or vice versa), thereby, forming the radiative exciton. If the concentration of freely moving excitons is high in single components materials, the collision of two excitons leads to exciton – exciton annihilation (Sokolik I. et al, 1996). However, if the excitons are rapidly trapped in the dopants, then the concentration of freely moving excitons and thus their annihilation probability is considerably reduced and quantum efficiency of OLED increases. Further active more, an additional advantage of doping a host with fluorescent molecules is that it provides an effective means to tune the emission colour of OLED. For example, using of blue fluorescent host, the entire visible spectrum is accessible simply by using an admixture of different guests into the emissive layer of OLED (Hosokawa et al, 1997).

3. SECOND GENERATION OLEDs: PHOSPHORESCENT OLEDs

Although highly fluorescent dyes increase the EL efficiencies of small-molecule OLEDs, they are able to harness only a fraction of all electrically generated excitons. When electrically injected carriers recombine two types of excitons are formed: singlet excitons with total spin $S = 0$ and triplet excitons with total spin $S = 1$. As the ground state of organic molecules has $S = 0$, and the relaxation of a molecule through the radiative recombination of an exciton must conserve spin, fluorescent emission from singlet excitons is the only allowed process that generates photons. Thus, for typical fluorescent-based OLEDs, all triplet excitons are wasted. For small-molecule devices, only 25% of the emissive singlet excitons are formed during electrical excitation, and therefore, the maximum internal quantum efficiency of fluorescent devices is 25%. However, there are some materials which exhibit light emission also from triplet excitons. In such materials, the singlet and triplet states are mixed due to the spin-orbit coupling and therefore the excited triplet states share some singlet character and radiative decay to the ground state is allowed. This process is known as phosphorescence. Adding a heavy metal atom such as platinum, iridium, etc. to an organic fluorescent material increases the spin-orbit coupling that mixes singlet and triplet excited states, which allows the efficient radiative decay of triplet excitons (Ikai, *et al* 2001 and Adachi *et al* 2001).

Fig. 3 shows the schematic energy level diagram of an optimized small molecule OLED employing the phosphorescent complex $[\text{Ir}(\text{ppy})_3]$ doped into CBP host (Baldo et al 1999). The Inset shows the chemical structural formulas of (a) $[\text{Ir}(\text{ppy})_3]$, (b) CBP, and (c) BCP. Fig. 4 shows the simplified illustration of different transfer processes from the host to the guest. Förster energy transfer between singlet states and Dexter energy transfer from the host to the guest triplet states are shown. In this case, two ETL layers are used—one (CBP) hosts the phosphorescent iridium complex and one (BCP) acts solely as a hole (and exciton) blocking layer. Upon injection, holes are transported in the HTL and recombine with the electrons that have been injected into the hole blocking layer and have drifted to the CBP ETL. Both singlet and triplet excitons are formed in the CBP host and then both types of excitons are transferred nonradiatively to the emissive state of the iridium complex. This state then emits light through phosphorescence. The net effect is that both the singlet and triplet excitons created in CBP are utilized for light emission. While purely singlet exciton emission provides an upper limit on the internal quantum efficiency of ~25%, nearly 100% internal efficiency OLEDs have been demonstrated employing this iridium complex (Adachi et al 2001).

Although there is some controversy regarding the fraction of emissive singlet excitons formed in polymeric systems (Kohle et al 2002) efforts have nevertheless been made to blend efficient phosphorescent small molecules into

polymers to try to make use of the triplet excitons (Kawamura et al 2002 and Vaeth et al 2002). To date, the observed efficiencies in these hybrid systems remain below those described for small molecule phosphorescent OLEDs, presumably due to incomplete energy transfer and lack of exciton confinement. However, it is believed that the further materials development will provide efficient harnessing of triplet excitons in PLEDs, which will enable solution processible devices with 100% internal efficiency.

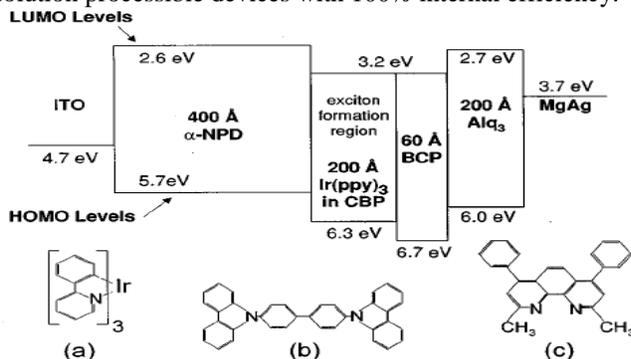


Fig.3 Schematic energy level diagram of an optimized small molecule OLED employing the phosphorescent complex [Ir(ppy)₃] doped into CBP host. The Inset shows the chemical structural formulas of (a) [Ir(ppy)₃], (b) CBP, and (c) BCP (after Baldo et al., 1999.).

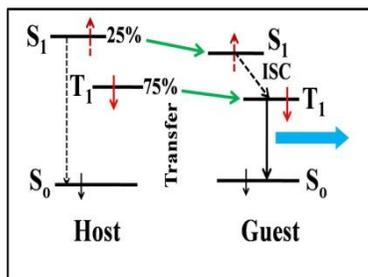


Fig. 4 Simplified illustration of different transfer processes from the host to the guest. Förster energy transfer between singlet states and Dexter energy transfer from the host to the guest triplet states are shown.

A problem common to all OLEDs, particularly phosphorescent OLEDs is the rapid drop in power efficiency with increasing brightness due to either second-order excitonic processes or ohmic losses in the transport layers or at the contacts. These ohmic losses have typically limited small molecule OLED drive voltages to higher than 5 V. Recently however, doping transport layers with either donor or acceptor type materials has led to significant increases in film conductivities and hence concomitant decreases in drive voltage and display brightnesses are now achievable at 2.6 V in the green. Starting with the OLED shown in **Fig. 3**, doping the electron transport layer with alkali metals such as Li and doping the hole transport layer with a strong organic acceptor such as **F4-TCNQ** (tetrafluorotetracyanoquinodimethane) was used to demonstrate (Pfeiffer et al 2002). OLEDs operating with efficiencies in excess of 25 lm/W at brightnesses required for lighting applications—10X that required for display applications. In the near future, it is likely that higher efficiencies at high brightness will be obtained as more research groups begin to develop and optimize new device architectures that exploit this doping concept.

In the PL process of phosphorescent molecules, an electron is excited from S_0 to S_1 or any other singlet state from where it rapidly thermalizes into S_1 (Fig. 4). Then from S_1 it undergoes intersystem crossing (ISC) to the triplet state T_1 with a probability P_{isc} . Finally, it can decay from T_1 to S_0 radiatively or non-radiatively with a rate constant δ_1 and δ_2 respectively. Thus, the efficiency for phosphorescent PL can be expressed as

$$\eta_p = P_{isc} \frac{\delta_1}{(\delta_1 + \delta_2)} \quad (3)$$

In the case of EL, the situation is different. Due to the electrical excitation, both singlet and triplet excitons are directly created on either the guest or host molecules with a statistical splitting of $\gamma_{st} = 25\%$ singlet and $(1-\gamma_{st}) \sim 75\%$ triplets. If the concentration of guest molecules in a host molecular matrix is sufficiently high and a suitable matching of the energy levels to enable energy transfer, is available, it can be assumed that all excitons generated on matrix molecules will completely transfer their energy to the guest within their lifetime. Accordingly, the internal quantum efficiency of EL is given by

$$\eta_{EL} = [(1 - \gamma_{st}) + \gamma_{st} P_{isc}] \frac{\delta_1}{(\delta_1 + \delta_2)} \quad (4)$$

Thus, it is evident that η_{EL} will be at least 75%, if $\frac{\delta_1}{(\delta_1 + \delta_2)}$ is close to unity.

In recent years, phosphorescent OLEDs with internal quantum yields of nearly 90% have been demonstrated using $\text{Ir}(\text{ppy})_3$ (Ikai M., et al 2001) or $(\text{ppy})_2\text{Ir}(\text{acac})$ (Adachi C. et al 2001). A general problem involved in phosphorescent OLEDs is that its efficiency decreases more severely at higher brightness level as compared to that of a fluorescent OLED. This is caused as a result of the longer lifetime of triplet excitons (typically 500 ns to 100 μs) in phosphorescent materials as compared with that of singlet excitons ($\sim 10\text{ns}$), which leads to triplet annihilation or quenching of triplet excitons by charge carriers at high brightness (Baldo et al., 2000). The effect of annihilation can be reduced by designing phosphorescent molecules with short lifetime, i.e., with a large spin-orbit coupling. An alternative approach is to co-dope the host with a phosphorescent sensitizer and fluorescent emitter. In this case, long-lived triplet states are avoided by fast and efficient resonant Förster transfer from the triplet state of the sensitizer to the singlet state of the emitter. In fact, the long lifetime and accordingly long diffusion length require device architectures consisting of exciton blocking layers, which eliminate the quenching at contact or at interface.

It is to be noted that the price one has to pay for the increased efficiency in phosphorescent OLEDs, is the energy loss in the transition from singlet to triplet state. In fact, for a given emission wavelength this requires host materials having wider band gap. In the case of the emission at longer wavelengths, for example, in the case of green phosphorescence emission, resonant exothermic energy transfer takes place from both the host singlet and triplet states to the phosphor. However, when triplet energy of the phosphor increases, it becomes difficult to find a suitable host with an appropriate high energy triplet state. In this connection, one route to efficient blue electrophosphorescence involves the endothermic energy transfer from a near-resonant excited state of the host to the higher triplet energy of the phosphor (Baldo et al., 1999). This process can be very efficient if the energy required in the transfer is not significantly greater than the thermal energy (Pfeiffer et al., 2003). The occurrence of recombination predominantly from a high energy phosphor state in quasi-equilibrium with a low energy host singlet state appears surprising. This becomes possible because the triplet lifetime of the phosphor dopant is significantly less as compared to the forbidden triplet transition of the fluorescent conductive host. For example, with 4, 4'-N,N'-dicarbazole biphenyl (CBP) as a host (triplet energy 2.56eV) and Flrpic as guest (triplet energy 2.62 eV), a maximum internal electroluminescence quantum efficiency of $\sim 5.7\%$ and a luminous power efficiency of 6.3 lm/W have been achieved (Adachi et al, 2000). This fact clearly demonstrates significant improvement over efficiencies of blue fluorescent emitters reported till now.

4. THIRD GENERATION OLEDs: OLEDs BASED ON THERMALLY ACTIVATED DELAYED FLUORESCENCE (TADF)

Recently, Adachi and his co-workers (Uoyama et al. 2012) of Kyushu University, Fukuoka, Japan, have reported a class of metal-free organic electroluminescent molecules in which the energy gap between the singlet and triplet

excited states is minimized by design, thereby promoting highly efficient spin up-conversion from non-radiative triplet states to radiative singlet states while maintaining high radiative decay rates of more than 10^6 decays per second. In other words, these molecules harness both singlet and triplet excitons for light emission through fluorescence decay channels and provides an intrinsic fluorescence efficiency in excess of 90 per cent and a very high external electroluminescence efficiency of more than 19 per cent, which is comparable to that achieved in high-efficiency phosphorescence-based OLEDs. Adachi and his co-workers (Uoyama et al. 2012) have designed a series of highly efficient thermally activated delayed fluorescence (TADF) emitters based on carbazolyl dicyanobenzenes (CDCBs), with carbazole as a donor and dicyanobenzene as an electron acceptor. The fluorescent OLEDs are called first generation OLEDs, the phosphorescent OLEDs are called second generation OLEDs, and the thermally activated delayed fluorescent OLEDs are called third generation OLEDs. Fig. 5 shows the performance of OLEDs containing CDCB derivatives. Fig. 6 shows the external electroluminescence quantum efficiency as a function of current density for OLEDs containing 4CzIPN, 4CzTPN:Ph as emitters. Inlet illustrates the electroluminescence spectra of the same OLEDs at a current density of 10 mA cm^{-2} (after Uoyama et al. 2012).

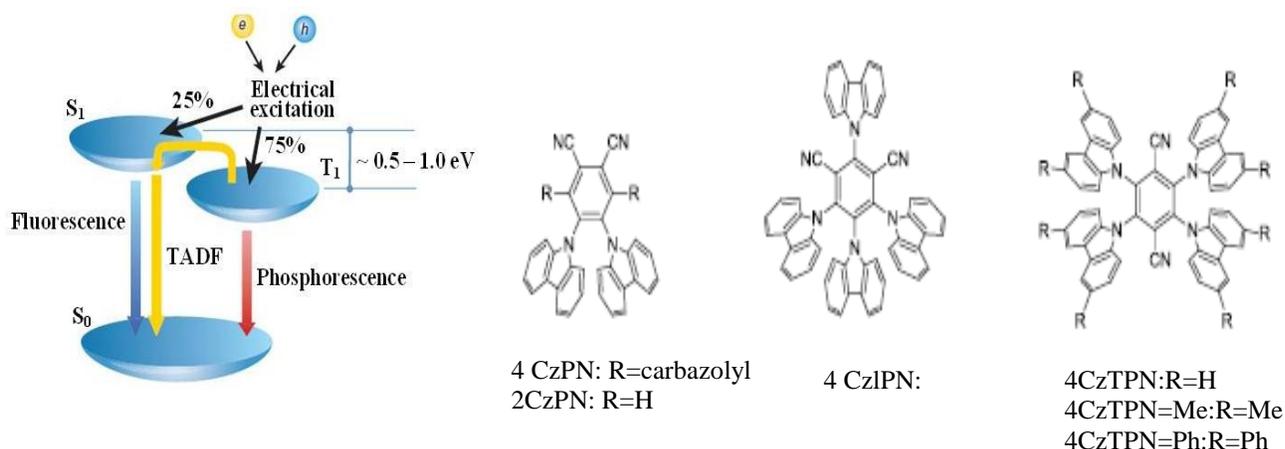


Fig. 5 | Energy diagram and molecular structures of Carbazolyldicyanobenzenes (CDCBs). a, Energy diagram of a conventional organicmolecule. b, Molecular structures of CDCBs.Me, methyl; Ph, phenyl. (after Uoyama et al. 2012).

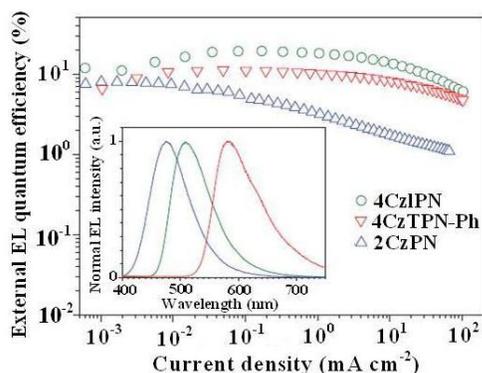


Fig. 6 Performance of OLEDs containing CDCB derivatives. External electroluminescence quantum efficiency as a function of current density for OLEDs containing 4CzIPN (green circles, error within 1.5 %), 4CzTPN:Ph (red triangles, error within 1 %) as emitters. Inlet, electroluminescence spectra of the same OLEDs (coloured accordingly) at a current density of 10 mA cm^{-2} (after Uoyama et al. 2012).

5. CONCLUSIONS

In fluorescent OLEDs the maximum Internal Quantum Efficiency is 25% because only the singlet excitons emit light. The use of phosphorescent heavy metal-organic complexes exploits the normally non-radiative triplet excitons and so enhances the overall Internal Quantum Efficiency to 100 %. Recently, a new class of metal-free organic electroluminescent molecules have been reported, in which the molecules harness both singlet and triplet excitons for light emission through fluorescence decay channels and provides an intrinsic fluorescence efficiency in excess of 90 % and a very high external electroluminescence efficiency of more than 19 %, which is comparable to that achieved in high-efficiency phosphorescence-based OLEDs. Thus, great advances have been made in the development of materials for OLEDs.

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