ADVANCED MATERIALS

Mixing of Excimer and Exciplex Emission: A New Way to Improve White Light Emitting Organic Electrophosphorescent Diodes**

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In the past two decades a significant research effort has focused on the photophysical properties of advanced organic materials for optoelectronic devices. Examples include the development of organic white light emitting diodes (WLEDs) since they are at the heart of display technology[1] and offer potential applications as novel lighting sources that are less expensive and more efficient than conventional incandescent and fluorescent illumination sources.[2–4] The most impressive characteristics of organic WLEDs are those based on single emissive dopant, where molecular excitons are harnessed to form triplet excimers.[5–8] They combine molecular phosphorescence with the red-shifted excimer phosphorescence that yields the emission approaching white light. Here, we use electron donor-electron acceptor emitter layers, in which broad emission band of an exciplex mixes with excimer emission, enabling us to form an efficient white device with particularly high color rendering index of CRI = 90.

One of the most stormily developing classes of organic photonic devices nowadays are organic light-emitting-diodes (LEDs).[1] Among them, white-light-emitting-diodes (WLEDs) are of particular interest because they offer low-cost alternatives for back-lights in flat panel displays and are considered as future illumination sources which are able to operate at low voltages with high luminance efficiency.[2–4] By definition, the emission spectrum of WLEDs must cover possibly uniformly the whole visible spectrum of electromagnetic radiation. Several routes have been employed to realize this goal, the fabrication of stacked[3] or multilayer[9] LED structures with separated molecular emitters, that is blue, green and red,

was proposed initially. Recently, a high-performance organic WLED has been fabricated that exploits three different emitters mixed together in one emissive layer to get stable color balance at a high external electroluminescence (EL) quantum efficiency (QE) of 11 % photons/electron (ph/e) and color rendering index CRI = 85.[10] The blue fluorescence of a dye dopant was mixed with green and red emissions of two phosphorescent dopants. However, this approach requires a very careful adjustment of the concentration of each dye because energy transfers from the higher energy blue dye to the green dye and from the green dye to the red dye. A simplification of the device structure can be achieved by combining molecular (monomer) and excimer phosphorescence from one emitter doped in a single emissive layer.[5,7,8] Single dopant WLEDs give voltage independent white emission with external EL QE as high as 16 % ph/e[7,8] but, due to the excessive distinctiveness of individual components in the structured emission spectra, their CRIs do not exceed 75.[5,7,8]

In efforts to improve the WLEDs based on a combination of monomer and excimer spectra, we now report the achievement of well balanced efficient white emission from a single emissive layer comprised of an electron donor (D) and an electron phosphorescent acceptor (A) which are able to create exciplexes revealing the broad emission spectrum located between monomer and excimer spectra of the phosphor. Such prepared emissive layers utilize emission from three different emitters (but one phosphorescent dopant) that renders the combined light output to cover the visible spectrum more uniformly and leads to CRI factor as high as 90 with a high external EL QE ≈ 7 % ph/e.

The emissive layer (EML) of the WLED reported here consists of a bluish-green emitting phosphor, selected from a group of highly efficient N C N-coordinated platinum(II) complex phosphors, platinum [methyl-3,5-di-(2-pyridyl) benzoate] chloride (PtL^2Cl) electron acceptor,[11,12] and (4,4′,4″-tris(*N*-(3-methylphenyl)-*N*-phenylamino)triphenylamine) (m-MTDATA) electron donor, co-evaporated in vacuo in a molecular proportion 1:1 on a hole-transporting layer (HTL) of *N,N*′-diphenyl-*N,N*′-bis(3-methyl)-1,1′-biphenyl-4,4′-diamine (TPD) blended with a polycarbonate (PC) binder on a transparent indium-tin-oxide (ITO) hole injecting electrode. Figure 1 shows the absorption and PL spectra of the two different composition EMLs and their material components. It is apparent that unlike the PL material component spectra, the emission from the EMLs shows up as the broad band spectra characteristic of triplet $^3|$PtL^2Cl:PtL^2Cl⟩* excimers[13] and $^3|$m-MTDATA:PtL^2Cl⟩* exciplexes,[14] respectively. Although the terms excimer and

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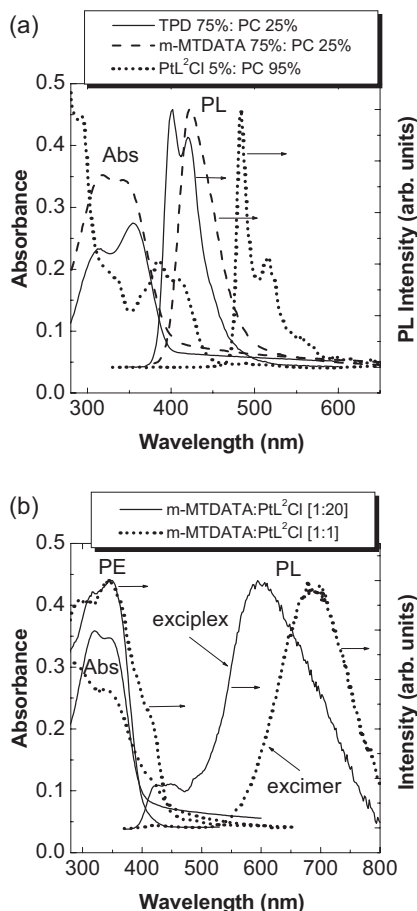
Figure 1. Absorption (Abs) and photoluminescence (PL) spectra of single active components films (a) and their two blends (D:A) dominated by the acceptor (1:20) and balanced donor-acceptor molecular concentrations (1:1) (b). A difference between the triplet excimer phosphorescence characteristic of excited acceptor complex $^3\lvert\mathrm{Pt}L^2\mathrm{Cl}:\mathrm{Pt}L^2\mathrm{Cl}\rangle^*$ and triplet exciplex phosphorescence characteristic of donor–acceptor $^3\lvert\mathrm{m\text{-}MTDATA}:\mathrm{Pt}L^2\mathrm{Cl}\rangle^*$ exciplex, is apparent. Here, the PL has been excited at $\lambda_{exc} = 350$ nm. In addition, the photoexcitation spectra (PE) observed at the maxima of the excimer (dashed curve) and the exciplex (solid line) emission spectra are displayed in part (b) of the figure.

exciplex apply to excited (AA)* and (DA)* complexes that are formed in solution from the combination of an excited acceptor A* and its ground state monomer A, and an excited donor D* (or A*) and ground state monomer A (or D), respectively, normally under diffusion control, the emission from our film structures clearly emanates from a similar species. Their photoexcitation spectra (PE), shown in Figure 1b, provide evidence of direct sensitization of the excimer and exciplex like emission via the $^1\pi$–π^* excited state of the acceptor and donor molecule, and the resulted monomer exciton diffusion within the emissive layer. The absorption and excitation spectra are not significantly different and resemble the absorption spectrum of the individual acceptor–donor components of the DA system. Thus, there is no compelling evidence for the presence of the ground-state AA associates or CT complexes.

The WLED architecture utilizes an electron-transporting (ETL)/hole blocking layer of 3-phenyl-4-(1′-naphthyl)-5-phenyl-1,2,4-triazole (TAZ) and an electron blocking layer of 4,4′-*N*,*N*′-dicarbazole-biphenyl (CBP) or 1,1-bis(-tolylamino-phenyl) cyclohexane (TAPC) to confine carriers and excitons to the desired luminescence layer (m-MTDATA:PtL^2Cl). A calcium layer serves as an electron injection electrode (see Fig. 2).

The principle of device operation is illustrated in Figure 3. Holes and electrons injected from ITO$^+$ and Ca$^-$ electrodes, respectively, and transported through the HTL and ETL, recombine in the EML of the device, forming various excited states. The EML is unique in that three different emissive states are produced efficiently at the same time: (i) molecular excitons of the acceptor (^{3}A*) producing monomer phosphorescence,[12] (ii) triplet excimers ^{3}(AA)* = excited homo-molecular dimer of the acceptor (PtL^2Cl) that falls apart in the ground state, producing excimer phosphorescence,[8,13] and (iii) excited hetero-molecular dimer [exciplex ^{3}(DA)*] formed between molecules of the donor (m-MTDATA) and the acceptor (PtL^2Cl), which, like excimer, does not exist in the ground state and produces exciplex phosphorescence.[14] However, their contributions to the resulting emission spectrum vary with the material of the spacer (10 nm) between HTL and EML (see Fig. 2). Figure 4 provides evidence for such a difference by comparing the EL spectra of two devices operated at a voltage $U = 22$ V. Device I has a 10 nm-thick CBP spacer placed between the (TPD:PC) HTL and the (m-MTDATA:PtL^2Cl) EML, whereas device II has a 10 nm-thick spacer made of TAPC. Although both EL spectra are dominated by the broad band emission from the exciplex, its contribution is of 33 % larger in the EL spectrum of device II as compared with that of device I. Furthermore, they show different sensibility to the applied field (see Fig. 5). Since the composition and the rest of the device architecture are the same, we assign the difference in the properties of the EL spectra from these devices to the difference in the electronic affinity (LUMO) and the ionization potential (HOMO's energies) of the spacer materials (see Fig. 2). Due to a great difference in the energy barrier, the electrons much easier penetrate CBP than TAPC layer, enabling their recombination at the (TPD:PC)/CBP interface, where ^{1}TPD* molecular excitons are formed and contribute to the total EL spectrum in the violet at the expense of the remaining components of the spectrum. At high voltages its contribution can reach a value of 5 % while at a reduced voltage it substantially drops down changing the optical characteristics of device I as demonstrated in Figure 5a. In order to enter CBP the holes must overcome a barrier of 0.6 eV, whereas this value drop down to 0.1 eV at the interface (TPD:PC)/TAPC. This allows holes to freely penetrate the TAPC layer and reach contact with the EML. There, holes localized on TAPC molecules (TAPC$^+$) form electron–hole pairs (TAPC$^+$:PtL^2Cl$^-$) with acceptor-located electrons (PtL^2Cl$^-$). The energy of the electron–hole pair is determined by the difference between the ionization energy of the donor (I_D) and electron affinity of the acceptor
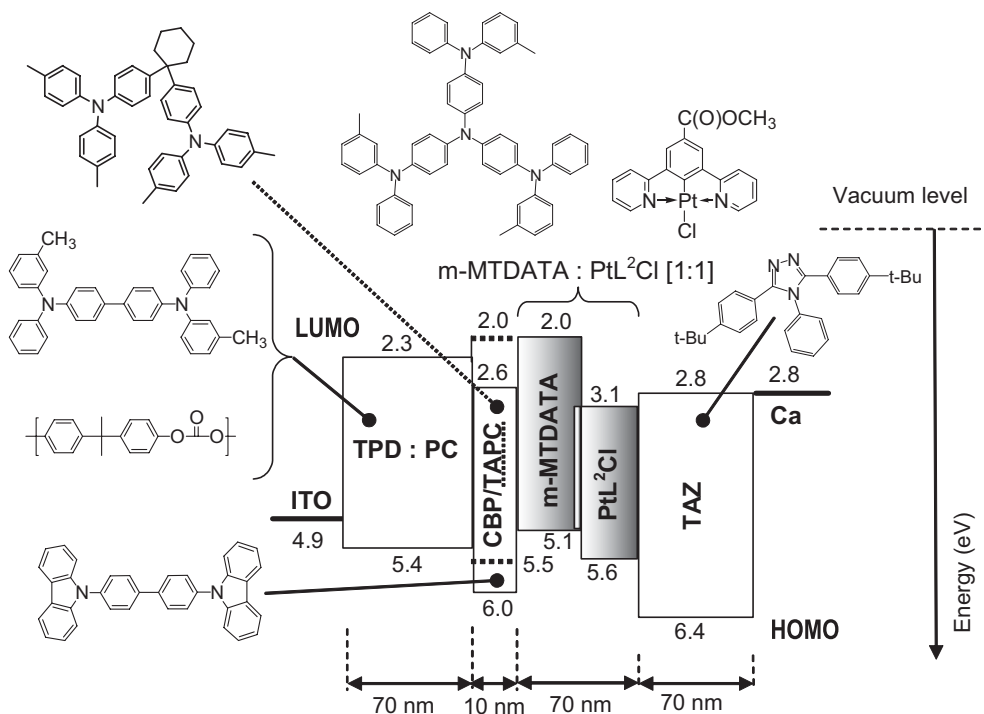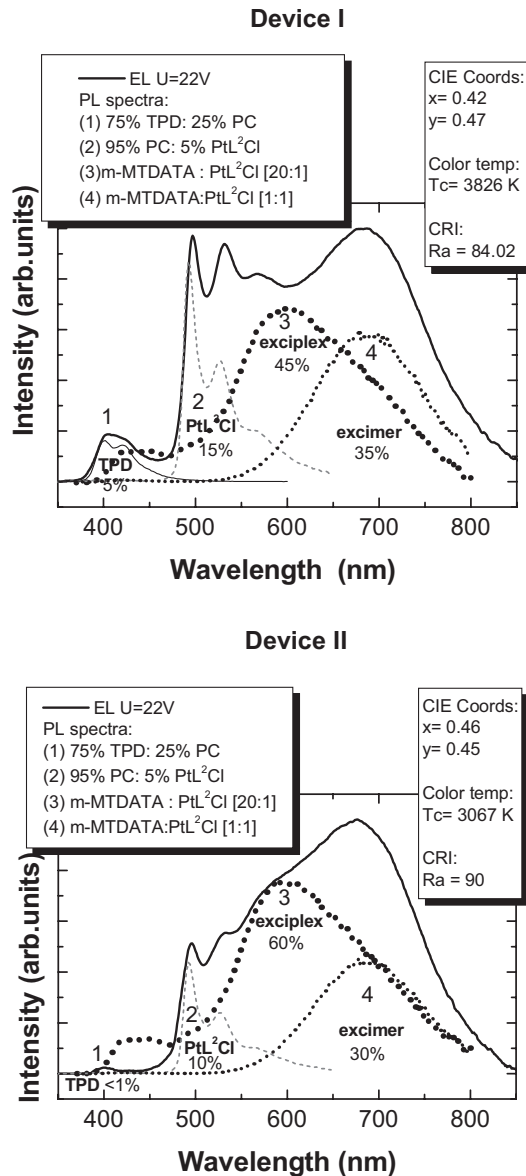
Figure 2. The architecture of the EL devices studied, and molecular structures of the materials used (for chemical names see text). The highest occupied molecular orbital (HOMO) obtained for each material corresponds to its ionization potential. The lowest unoccupied orbital (LUMO) is equal to the molecular electronic affinity. The Fermi level positions for ITO and Ca electrode contacts are added for completion. The positions of all the levels are indicated by the numbers in electronvolts relative to the vacuum level at energy zero. Two devices have been examined: device I with a 10 nm-thick spacer of CBP, and device II with a 10 nm-thick spacer of TAPC; the spacer materials differing in HOMO and LUMO. The remaining components of the architecture are the same for both devices.
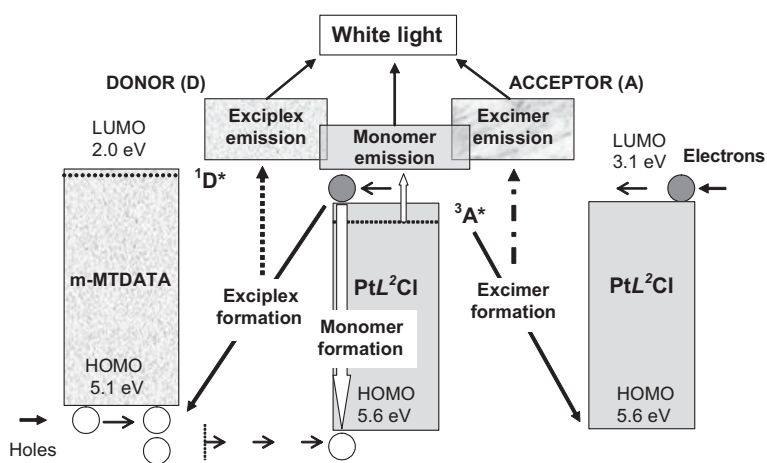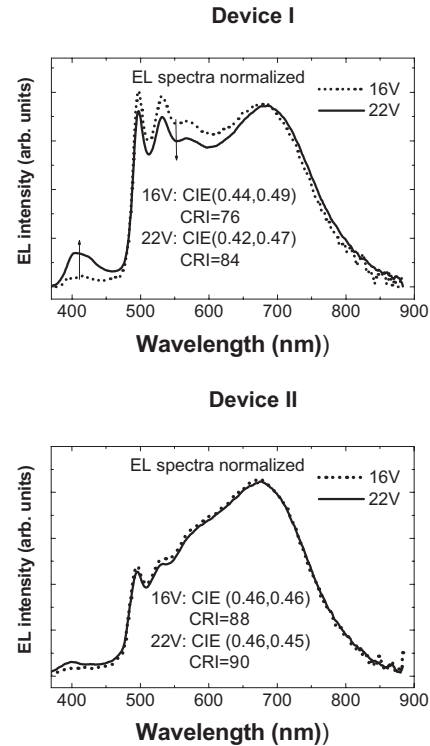

Figure 3. Proposed generation mechanisms of white light in an organic LED based on a hole transporting material (here, m-MTDATA) acting as an electron donor (D) to an electron acceptor (A) molecule of an organic phosphor (here, PtL^2Cl) mixed in an emissive layer, D:A (here, 1:1). The monomer phosphor triplets (^{3}A*), their combination with ground state phosphor acceptor molecules [triplet excimers, ^{3}(AA)*], and excited hetero-dimer [^{3}(DA)*] are generated throughout all the emissive layer of both device I and device II (see Fig. 2). Mixing their emissions that span from bluish-green to red, yields white light with a color rendering index CRI = 84 for device I. The CRI index improves up to CRI = 90 for device II, where the contribution from monomer and excimer emissions becomes diminished due to a radiationless recombination of PtL^2Cl - located electrons with TAPC-located holes at the spacer/EML interface, and the EL spectrum is much stronger dominated by the emission of exciplexes than that in device I (see Fig. 4).

(A_A),[15] $E_{e-h} = I_D - A_A \approx 5.5 - 3.1$ eV $= 2.4$ eV. Since no new exciplex emission is observed in this energy region, and E_{e-h} is too low to excite the acceptor triplet (2.6 eV), a possibility of electron transfer from PtL^2Cl$^-$ to a more electronegative entity (chemical or physical defect) in TAPC and the formation of an emissive electromer at ≈ 580 nm[16] may be an alternative for the decay of the pair. But no emission occurs at 580 nm even with a single (TAPC 95 %: PtL^2Cl 5 %) emissive film. The pairs most likely decay by a radiationless recombination process, lowering the population of emissive molecular triplets ^{3}(PtL^2Cl)* and hence of emissive excimers, $^3|$PtL_2Cl:PtL_2Cl$\rangle$*. The EL spectrum becomes strongly dominated by the exciplex emission resulting in a color rendering index of CRI = 90 which is the highest CRI among the reported values for excimer-based organic WLEDs. Only recently, a CRI of 90.4 has been reported for WLEDs based on the emission from a combination of exciplexes with different acceptors,[17] but their efficiency is not specified (cf. Table 1). To get the exciplex spectrum located suitably between the spectra of the monomer and the excimer emission for a given phosphor, one has to choose properly the donor. For the phosphor used, PtL^2Cl, it is ex-

Device I

Intensity (arb.units)

EL U=22V
PL spectra:
(1) 75% TPD: 25% PC
(2) 95% PC: 5% PtL^{2}Cl
(3) m-MTDATA : PtL^{2}Cl [20:1]
(4) m-MTDATA:PtL^{2}Cl [1:1]

CIE Coords:
x= 0.42
y= 0.47

Color temp:
Tc= 3826 K

CRI:
Ra = 84.02

3 exciplex 45%
4
2 PtL^{2}Cl 15%
excimer 35%
1
TPD 5%

Wavelength (nm)

Device II

Intensity (arb.units)

EL U=22V
PL spectra:
(1) 75% TPD: 25% PC
(2) 95% PC: 5% PtL^{2}Cl
(3) m-MTDATA : PtL^{2}Cl [20:1]
(4) m-MTDATA:PtL^{2}Cl [1:1]

CIE Coords:
x= 0.46
y= 0.45

Color temp:
Tc= 3067 K

CRI:
Ra = 90

3 exciplex 60%
2 PtL^{2}Cl 10%
4 excimer 30%
1
TPD <1%

Wavelength (nm)

Figure 4. The electroluminescence spectra (solid lines) for device I and device II (see Fig. 2), recorded at a voltage of $U = 22$ V. They are composed of three essential bands corresponding to the photoluminescence (PL) spectra of molecular triplet emission of PtL^{2}Cl (line 2), triplet exciplex emission of m-MTDATA:PtL^{2}Cl (line 3) and excimer emission of PtL^{2}Cl (line 4) with a small contribution from the molecular singlet emission of TPD, ^{1}D*, (line 1). They appear as a number of characteristic features in the EL spectrum. Their percentage contribution to the EL spectrum by the area under the curves is given for both devices. The EL spectrum of device II differs from that of device I, resulting in a reduced color temperature (T_c), but an increased CRI index as indicated in the right-up corner insets. The reason is the (PtL^{2}Cl$^-$ + TAPC$^+$) radiationless recombination process at the TAPC spacer/EML interface, diminishing the contribution of the monomer and excimer emissions to the EL spectrum (for explanations see text).

pected to be a material with a relatively low ionization potential. There are not too many of them and, therefore, it is a challenge to chemists to synthesize such new compounds. On

Device I

EL intensity (arb. units)

EL spectra normalized
····· 16V
—— 22V

16V: CIE(0.44,0.49)
CRI=76
22V: CIE(0.42,0.47)
CRI=84

Wavelength (nm))

Device II

EL intensity (arb. units)

EL spectra normalized
····· 16V
—— 22V

16V: CIE (0.46,0.46)
CRI=88
22V: CIE (0.46,0.45)
CRI=90

Wavelength (nm))

Figure 5. The EL spectra of device I and device II at two different voltages (16 V and 22 V). The values of CIE coordinates and CRI indexes corresponding to the spectra are given under the curves. A practically voltage independent EL spectrum is observed for device II.

the other hand, an efficient phosphor with still higher electronic affinity can be used with donors having a higher ionization potential. So, to fabricate a good optical quality monomer-excimer-exciplex (MEE) WLED one cannot use any combination of electron donors and electron acceptors, but still there is remarkable range of electronic levels allowing to combine different donor and acceptor to realize a quite remarkable diversity of good MEE WLEDs.

Performance characteristics of the WLEDs studied are shown in Figure 6. The TAPC spacer containing WLED (device II) gives a maximum external EL QE of (6.5 ± 0.5) % ph/e at low brightness levels ($L = 0.1$ Cd m^{-2}) and (3.0 ± 0.5) % ph/e at a luminance $L = 500$ Cd m^{-2}. The voltage (thus driving current) dependence of the EL spectra (cf. Fig. 5) have been accounted for in the calculation of the EL QE, the corrections factors for device II being practically negligible though. The decline in QE at large current densities, observed for both devices, is associated with monomer triplet-triplet annihilation and/or their field-dependent dissociation[14] accompanied by the dissociation of exciplexes.[19] Compared with previous single-dopant (monomer/excimer), high efficiency organic WLEDs, the present work devices have a less pronounced efficiency roll-off at high current densities. The current density at the point where QE has declined by half from its maximum value is > 5 times that of only monomer/excimer devices, while the EL turn on voltage falls in a similar range of values.

Table 1. Most advanced, selected performance characteristics of organic WLED structures

| Structure	φ_{ext} [% ph/e]	η_P [lm/W] (L) [cd/m^2]	CIE [a]	CRI [b]	Comments & references
Fluorescent/ phosphorescent	11.0	22.1 (500)	(0.38, 041)	85	maximum values [10]
Multiple phosphor-doped emitters	5.2	6.4	(0.37, 0.40)	83	maximum values [5] (L is not specified)
Phosphorescent triple-doped	12.0	26.0 (100)	(0.43, 0.45)	80	values at 10^{-3} mA/cm^2 (Ref. [18])
Phosphorescent triplet excimers	5.7	5.2 (500)	(0.40, 0.43)	81	maximum values [7] maximum values [8]
	15.5	9.5 (40)		< 60	
Phosphorescent triplet excimer/exciplex	6.5	9.0 (500)	(0.46, 0.45)	**90**	maximum values (this work)
Exciplex emission with mixed acceptors	–	– (425)	(0.32, 0.35)	90.4	no data for φ_{ext} and η_P are reported (Ref. [16])

[a] 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). [b] CRI = color rendering index; for ideal white light CRI = 100.

We note that the efficiency of the present device can be improved by using highly efficient acceptors and donors forming exciplexes with QE → 1.

We conclude that the use of electron donor and electron acceptor phosphor single dopant systems allows us to obtain highly efficient organic WLEDs with the color rendition approaching the CRI = 100 for ideal white light. The CRI index can be tuned by varying proportions of the monomer triplet, phosphor excimer and exciplex mixture emission components of the system, and its further improvement by varying electron donor-electron acceptor ratio and/or introducing electronically active spacers between hole-transporting and emissive layers of the device. Such WLEDS have potential for use in the new generation of sources for solid-state indoor lighting.

Experimental

Materials: The synthesis of the phosphor used Pt*L*^{2}Cl is described in detail elsewhere [11]. Other compounds purchased from Syntech (m-MTDATA, CBP) and Polysciences Inc. (M.W. 32 000–36 000 PC) were used as supplied. TAPC was kindly provided by Dr. P. Borsenberger (deceased) from Eastman Kodak Co. Solution photophysical characterization of the materials was carried out using
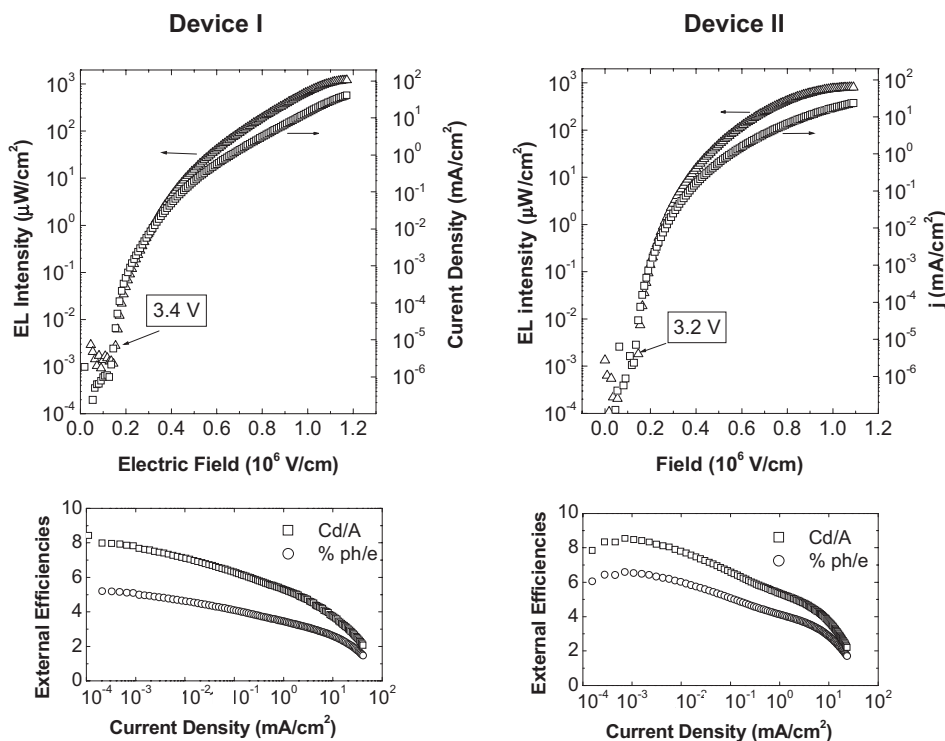
Device I   **Device II**

Figure 6. Performance characteristics of the WLEDs with different spacer materials, CBP (device I), and TAPC (device II) (cf. Fig. 1). Forward viewing EL intensity and current density as a function of applied electric field are shown in the upper part of the figure. EL turn on voltages are given in the insets. The two lower part figures show external quantum efficiency (open circles) and luminous efficiency (open squares) versus current density. The maximum external quantum efficiencies are φ_{ext} = (5.2 ± 0.5) % ph/e for device I, and φ_{ext} = (6.5 ± 0.5) %ph/e for device II.

a Jobin-YVON Fluoromax 2 spectrofluorimeter, and a Q-switched Nd:YAG-pumped system with a Hamamtsu R928 photomultiplier tube for the determination lifetimes. Solid state absorption and emission measurements were made using a Perkin Elmer Lambda 9 UV/Vis/NIR spectrometer and a StellarNet spectroradiometer, respectively, and a single-photon IBH Model 5000 counter was employed for the time-resolved luminescence measurements.

Device Manufacture: Devices were fabricated by spin coating the first layer on ITO glass substrate (20 Ω/square) and then vacuum depositing the overlying layers at a pressure of 0.05 mPa. The evaporation rate of CBP and TAPC layers was 0.2 nm s^{-1}, while the emitter layer was deposited from independent sources of m-MTDATA and PtL^2Cl with the evaporation rate of 0.1 nm s^{-1} by fine control of the evaporation sources coupled with independent thickness monitors. Each layer thickness was measured with a Tencor Alpha Step 200 profilometer. The current–voltage characteristics were measured with a Keithley Source-Measure unit, model 236, under continuous operation mode, while the light output power was measured with an EG&G power meter. All measurements were carried out at room temperature under argon atmosphere and were reproduced for many runs, excluding any irreversible chemical and morphological changes in the devices.

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