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M. Cocchi; D. Virgili; G. Giro; V. Fattori; P. Di Marco; J. Kalinowski; Y. Shirota

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Efficient exciplex emitting organic electroluminescent devices

M. Cocchi, D. Virgili, G. Giro, V. Fattori, and P. Di Marco
Institute of Photochemistry and High Energy Radiation, C.N.R., I-40129 Bologna, Italy

J. Kalinowski[a)]
Department of Molecular Physics, Technical University of Gdańsk, PL-80-952 Gdańsk, Poland

Y. Shirota
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Osaka 565-0871, Japan

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Organic electroluminescent (EL) single-layer (SL) and double-layer (DL) light-emitting diodes were fabricated based on 4,4′,4″-tris[3-methylphenyl(phenyl)amino] triphenylamine (m-MTDATA) and 2-(biphenyl-4-yl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) molecules incorporated in bisphenol-A-polycarbonate (PC) matrix. The external EL quantum efficiency of the dominating exciplex emission of the indium tin oxide (ITO)/m-MTDATA:PBD:PC/Ca SL structure is ≅0.4% photon/electron and that from the ITO/m-MTDATA:PC/PBD/Ca DL device exceeds 1% photon/electron. The operating voltage of the DL device at maximum efficiency is 4.8 V and the onset voltage of the EL is as low as 2.0 V. The photoluminesce quantum efficiency of the exciplex is greater than 17%. The high exciplex emission-based EL yield from the DL device is attributed to the narrow recombination zone imposed by the high energy barriers for the electron and hole transfer at the (m-MTDATA:PC)/PBD interface.
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In typical organic electroluminescent (EL) devices, light originates from radiative relaxation of well-localized molecular excited states formed by bimolecular recombination of electrons (e) and holes (h) injected from electrodes into single component organic layers, bilayers or blends.[1] Their EL quantum efficiency (φ_{EL}) is determined by the creation ability of singlet and triplet molecular excitons in electrofluorescing[2] and electrophosphorescing[3] devices, respectively, and by decay of these excited states including radiative relaxation represented usually by the photoluminescence (PL) quantum efficiency (φ_{PL}). With blend and bilayer devices, involving electron donor (D) and electron acceptor (A) entities, formation of exciplexes $[(D^{\star}A),(A^{\star}D),(D^{+}A^{-})^{\star}]$ may occur as a competitive pathway to the radiative relaxation of molecular excitons.[4–6] Moreover, if the formation of excited states is underlain by the bimolecular $e-h$ recombination process (as in organic EL), a Coulombically correlated ionic pair $(D^{+}\ldots A^{-})$ becomes a natural intermediate state. It may evolve to a less distant ion pair $(D^{+}-A^{-})$ which, in turn, may relax by the nonradiative or radiative cross transition reducing virtual population of molecular excitons and exciplexes. Their radiative relaxation produces a redshifted emission band called ''electroplex'' emission.[6–9] This generally results in multicomponent EL spectra and reduces the device performance. On the other hand, varying the ionization potential and/or electron affinity of electron donor and electron acceptor components of the EL devices enables tuning of their emission color.[5,6,9,10] The high electric fields operating in organic light-emitting diodes (LEDs) can alter the intensity ratio of the excimer emission band and that emanated from electroplexes $(D^{+}-A^{-})$ in cases where molecular dipole moment is large, an exciplex contains a large charge-transfer (CT) configuration component, or the $(D^{+}\ldots A^{-})$ pair forms an electroplex.[9] The effect is manifested by the electric field-driven tuning of the emission color either toward the blue[5] or the red.[6] The major problem in utilizing these effects in technological devices is finding systems that work with high exciplex emission efficiency.

In this letter, we report EL devices with efficient emission from exciplexes formed by donor molecules of 4,4′,4″-tris[3-methyl(phenyl)amino] triphenylamine (m-MTDATA) and acceptor molecules of 2-(biphenyl-4-yl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) dispersed in bisphenol-A-polycarbonate (PC) matrix in a single-layer (SL) device, and electron donor and electron acceptor molecules brought into the contact at the interface of a double-layer (DL) device that consists of the (m-MTDATA:PC) hole transport layer (HTL) and a 100% PBD as the electron transport layer (ETL). Unlike the low-efficiency exciplex emitting polymer EL devices,[4] the PL spectra of mixed $(D+A)$ films and EL spectra of present SL and DL LEDs practically do not show monomolecular emission from either electron donor and electron acceptor components.

The chemical structure of the materials, and their energy level diagram completed with the Fermi level positions for an indium tin oxide (ITO) anode and Ca cathode are shown in Fig. 1. The m-MTDATA was synthesized as reported earlier and purified by train sublimation.[11] The PBD was purchased from Aldrich, and PC of mW 32 000–36 000 from Polysciences Inc., and used as supplied. The (m-MTDATA:PBD:PC) films and (m-MTDATA:PC) HTLs were spin cast at 2000 rpm from a 10 mg/ml dichloromethane solution onto quartz substrates for absorption (Abs) and PL measurements, and onto ITO coated glass substrates (20 Ω/sq) for EL devices. The DL devices were completed by a

[a)]Author to whom correspondence should be addressed; electronic mail: kalino@polnet.cc

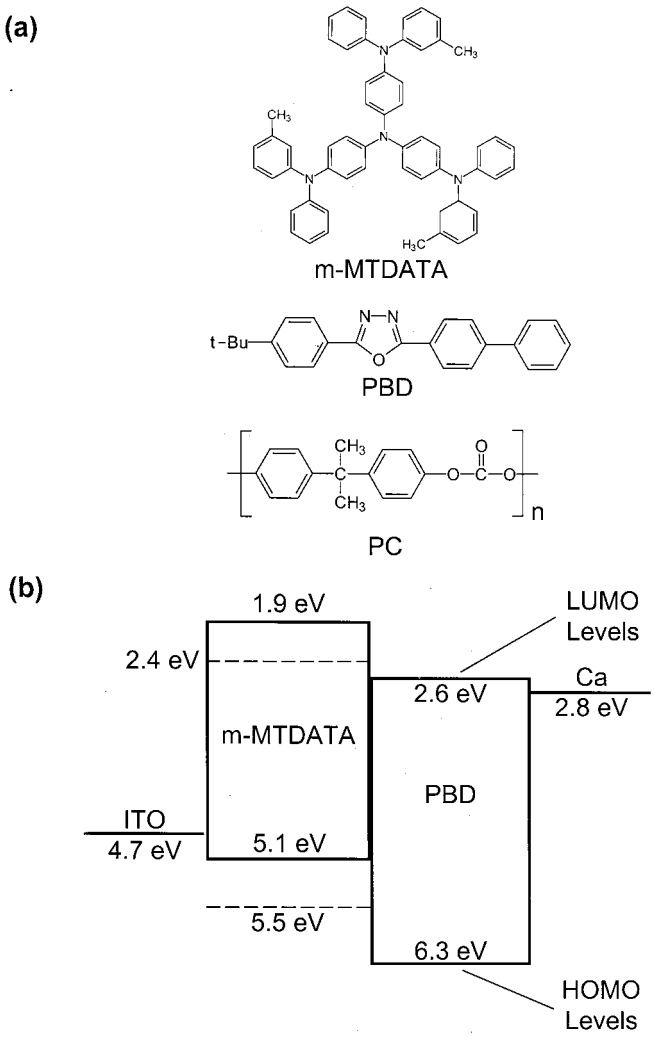

FIG. 1. Molecular structure (a) of the materials used in preparation of LEDs and energy level diagram (b) for the EL devices. Lowest unoccupied molecular orbital and highest occupied molecular orbital positions (dashed lines) for *N,N′*-bis(3-methylphenyl)-*N,N′*-diphenyl-[1,1′-biphenyl]-4,4′-diamine (TPD) are given for comparison in part (b).

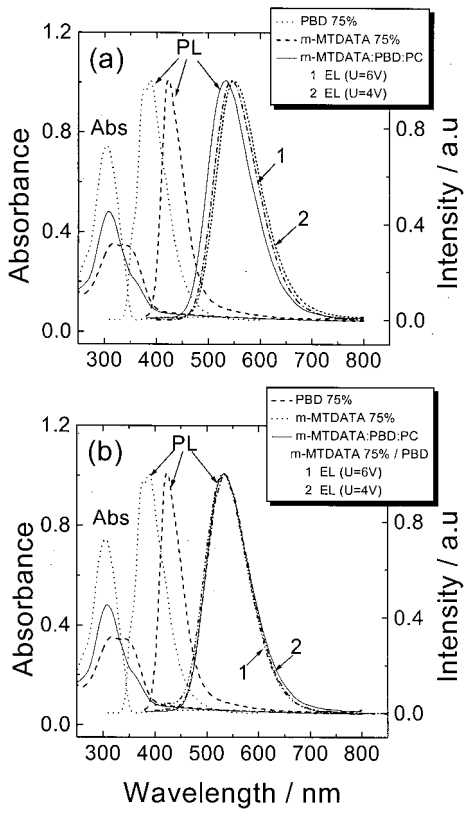

FIG. 2. EL spectra of a SL ITO/(40% m-MTDATA: 40% PBD: 20% PC) (60 nm)/Ca (a) and a DL ITO/(75% m-MTDATA: 25% PC) (60 nm)/100% PBD (60 nm)/Ca (b) device at different voltages. Abs and PL spectra excited with $\lambda_{exc}=300$ nm of (75% m-MTDATA: 25% PC), (75% PBD: 25% PC), and (40% m-MTDATA: 40% PBD: 20% PC) spin-cast films are given for comparison.

thermally evaporated 60 nm PBD ETL. The SL and DL organic systems were sandwiched by subsequent evaporation of a Ca electrode resulting in active device areas of $\cong 7\ \mathrm{mm}^2$. The absorption was measured with a Perkin Lambda 19 ultraviolet visible near-infrared spectrometer. The PL and EL measurements were made using an EG&G power meter and a Spex Fluorolog 2 spectrofluorimeter. The time-resolved PL measurements were made using a single-photon IBH Model 5000 counter. The current–voltage characteristics were measured with a Keithley Source-Measure unit model 236 under continuous operation mode. All characteristics have been reproducible for many runs excluding irreversible morphological changes in the samples. All measurements were conducted in an argon atmosphere.

Figure 2 shows the Abs and PL spectra of SLs of PC dispersions of m-MTDATA and PBD, their mixture, and the EL spectra of the SL and DL structures. The lack of any new absorption feature in the (m-MTDATA:PBD:PC) mixture implies that the new emitting species are not directly accessible from the ground state CT states, consistent with the assignment of an exciplex (EX). The maximum emission energy of CT EXs ($h\nu_{EX}$) can be evaluated from an empirical relationship using one-electron oxidation and reduction potentials,[12]

$$h\nu_{EX}(\mathrm{CT})=E^{ox}(\text{m-MTDATA})-E^{red}(\mathrm{PBD})-0.15\pm0.1\ \mathrm{eV}$$
$$=(0.31+2.01-0.15)\pm0.1\ \mathrm{eV}=2.2\pm0.1\ \mathrm{eV}, \quad (1)$$

where the oxidation potential of the donor, $E^{ox}(\text{m-MTDATA})=0.31$ eV, and the reduction potential of the acceptor, $E^{red}(\mathrm{PBD})=-2.01$ eV, were determined by cyclic voltammetry using the saturated calomel reference electrode in dichloromethane.

The value $h\nu_{EX}=2.3$ eV, following from the PL spectrum of the (m-MTDATA:PBD:PC) mixture [Fig. 2(a)], is in good agreement with the estimation in Eq. (1). However, two decay time constants, $\tau_{I}(22\%)=40$ ns and $\tau_{II}(78\%)=180$ ns, inferred from the two-exponential emission decay curve (Fig. 3), suggest the coexistence of two different emitting EX configurations. Though the long-time tail points of the decay curve are largely scattered, it is impossible to fit all the data with a single-exponential decay which in the semilogarithmic scale of Fig. 3 would show up as a single straight line over the applied time range. A difference in the PL and EL spectra of the SL structure [Fig. 2(a)] is a consequence of different excitation mechanisms. EX formation by bimolecular recombination of statistically independent holes and electrons in EL involves the intermediate species such as Coulombically correlated $e-h$ pairs $(D^{+}\ldots A^{-})$ and electroplexes $(D^{+}\text{-}A^{-})$.[6–9] These states must not be confused with the CT EX $(D^{+}A^{-})^{*}$ which requires short inter-

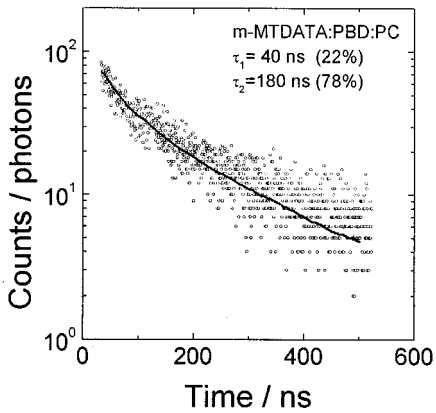

FIG. 3. Experimental PL decay curve for the dispersion of 40% of m-MTDATA and 40% of PBD in PC (points), and its best fit to the two-exponential decay with time constants τ_{I} and τ_{II} as given (solid line).

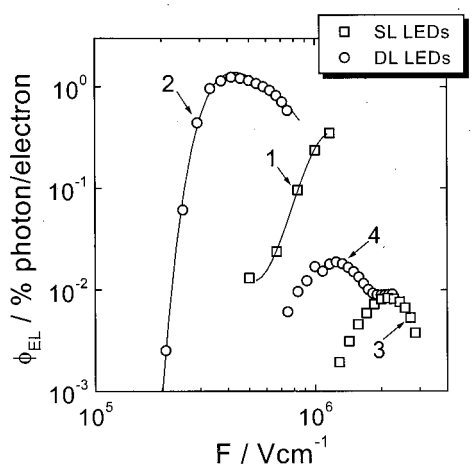

FIG. 4. External EL quantum efficiency as a function of applied electric field for the SL (1) and DL (2) structures from Fig. 2. The data for the ITO/(40% TPD: 40% PBD: 20% PC) (60 nm)/Ca (3) and for the ITO(75% TPD: 25% PC) (60 nm)/100% PBD (60 nm)/Ca (4) structures are shown for comparison (as adapted from Ref. 9).

molecular distances (<0.4 nm) and a large overlap intermolecular conformation.[13] The redshift of the EL spectra for the SL structure can be ascribed to the superposition of the EX emission and possible emission band originating from electroplex as observed for the SL (TPD:PBD:PC) EL devices.[6,9] One may wonder whether the difference between EL spectra of the SL and DL devices comes from a difference in their thickness, if they were considered as the microcavities with the ITO anode and Ca cathode forming the mirrors 60 nm and 120 nm apart, respectively. The resonance condition in such microcavities, $n_i d_i = m(\lambda/2)$[1], where n_i and d_i represent the refractive index and thickness of the ith layer (including a 150 nm-thick ITO layer), would lead to an enhancement of the emitted light at $\lambda_{\mathrm{SL}} \cong 402$ nm and $\lambda_{\mathrm{DL}} \cong 507$ nm as calculated with $n_{\mathrm{ITO}} = 1.92$, $n_{\mathrm{emitter}} = 1.9$, and $n_{\mathrm{ETL}} = 1.75$ (cf. Ref. 14) for the $m = 2$ mode perpendicular to the emitting surface. Thus, a possible microcavity effect, if any, would shift the DL device EL spectrum to the red as compared with that of the SL device. This is not the case in the present study as shown in Fig. 2.

The EL spectrum from the DL devices is entirely due to EX emission [Fig. 2(b)], with external quantum efficiencies exceeding 1% photon/electron at a luminance 1000 Cd m^{-2}. This value as compared to SL devices increases by a factor of three and over two orders of magnitude as compared with TPD-based DL devices. These relations can be seen in Fig. 4, where the external EL quantum efficiency as a function of applied field for various EL devices is displayed. The high EL quantum efficiency of the DL device is primarily due to charge confinement at the (m-MTDATA:PC)/PBD interface. Due to the high barriers for charge to cross the interface [see Fig. 1(b)], both electrons and holes are there closely confined. As the carrier transport through the (m-MTDATA:PC)/PBD interface is practically eliminated by high energy barriers, the observed current can be identified with the recombination current. Thus, the recombination zone should be limited to a nearest-neighbor donor and acceptor molecules that is should fall within $w \cong (2-3)$ nm. Using this value of w, the recombination probability $P_R = (1 - w/d) \cong 0.98$ can be evaluated.[1] This is not the case with the injection-controlled SL device, where up to about 60% of carriers decay at the electrodes and the $e-h$ recombination proceeds throughout the entire emitter thickness. The present EL results have been obtained with a lower bound on the quantum efficiency of the exciplex emission $\varphi_{\mathrm{PL}}(\mathrm{EX}) \cong 17\%$ as estimated by comparison of the PL output of the mixed film with that of a suitable layer of Alq_3 [taking $\varphi_{\mathrm{PL}}(Alq_3) = 25\%$],[2] under photoexcitation at $\lambda_{\mathrm{exc}} = 350$ nm. Clearly, the EL performance of the devices can be further improved by increasing φ_{PL}.

In summary, polycarbonate dispersions of m-MTDATA and PBD show both PL and EL spectra dominated by EX emission with a relatively high overall EL quantum efficiency as compared with a common donor TPD-based EL devices. The exciplex EL quantum efficiency from the (m-MTDATA:PC)/PBD heterojunction is greatly enhanced over the SL diode and exceeds by about two orders of magnitude that for the (TPD:PC)/PBD junction-based LEDs. This is due to high interfacial barriers for charge transport and resulting narrow recombination zone at the donor–acceptor material interface.

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