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Charge photogeneration effect on the exciplex emission from thin organic films

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The photoexcited singlet and triplet exciplex emission of thin photoconductive films containing an amine derivative *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) electron donor and the bathophenanthroline (BPT) electron acceptor drops largely with electric fields, falling down to about 20% of its zero-field value at high fields. This strong electric-field-induced exciplex emission quenching is interpreted in terms of the charge-imposed decay of singlet molecular excitons of TPD acting as precursors of the exciplexes and charge photogenerated on the TPD:BPT contacting sites. The favorable interrelation between the ionization potential of the donor and electron affinity of the acceptor leads there to an efficient field-enhanced exciton dissociation. The electrons trapped on acceptor molecules act in turn as charged exciton quenching centers. © 2006 American Institute of Physics. [DOI: 10.1063/1.2218821]

Understanding of the mechanisms underlying exciton decay, including the effect of high electric fields, is an outstanding challenge in organic optoelectronics. The most used examples are photovoltaic phenomena¹ and electroluminescence (EL).² According to energy considerations an exciton dissociation process in a molecular solid is greatly facilitated for electron donor (*D*)-electron acceptor (*A*) systems because the *A*-located electron (*A*⁻) and *D*-located hole (*D*⁺) form a (*D*⁺*A*⁻) charge pair with an energy (*E*_{ch}) which can be lower than the energy of its molecular singlet (*E*_S) or triplet (*E*_T) exciton precursors. The exciton energy surplus (*E*_{S,T} - *E*_{ch}) depends on the ionization potential of the donor (*I*_D) and electron affinity of the acceptor (*A*_A), the quantities that determine *E*_{ch} = *I*_D - *A*_A. The exciton dissociation occurs on the expense of the electron affinity of the acceptor molecule, largely compensating the attractive Coulomb interaction of the separated holes (h) and electrons (e). Clearly, such an effective channel for the photogeneration of charge competes with the formation of singlet ¹|*D:A** and triplet ³|*D:A** exciplexes created as a result of the excitonic (*D*^{*}*A* + *DA*^{*}) and charge transfer (*D*⁺*A*⁻ + *D*⁻*A*⁺) resonances following the interaction between excited (*A*^{*}, *D*^{*}) and ground state donor or acceptor molecules (*D*, *A*). Thus, the singlet exciplex-underlain fluorescence and triplet exciplex-underlain phosphorescence outcomes are determined by the trade-off between the exciton precursor decay due to the formation of exciplexes and the electric field dependent production of e-h pairs, the latter generating photocurrent. The fabrication of efficient exciplex light emitting diodes (LEDs), unlike photovoltaic cells, would then require a system minimizing the charge photogeneration. The electric-field-induced variation of the exciplex emission becomes a natural consequence of this dependence.

In the present work, we have investigated the photoluminescence (PL) response to high external electric fields ap-

plied through a combination of a high- and a low-work-function electrodes to thin film blends of a well-known electron donor of an amine derivative *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) and two electron acceptors molecules of bathophenanthroline (BPT) by itself or acting as a ligand to the Gd atom in its complex Gd(tmhd)₃BPT. The latter has been used to suppress the singlet component of the two spin state singlet and triplet exciplexes, ¹|TPD:BPT>* and ³|TPD:BPT)*, created by the excitonic resonance between the excited molecular donor singlets ¹TPD* and triplets ³TPD* and ground state acceptor ¹BPT, respectively.³

The molecular structures of the materials used and their energy level diagram completed with the Fermi level positions for an indium tin oxide (ITO) and Ca electrode contacts to apply an external electric field are shown in Fig. 1. The TPD and BPT were purchased from Aldrich, bisphenol-A-polycarbonate (PC) of molecular weight of 32 000–36 000 was purchased from Polysciences Inc., and all are used as supplied. The Gd(tmhd)₃BPT was synthesized and purified following the literature procedures.⁴ The highest occupied molecular orbital (HOMO) levels of all the compounds were here estimated from their oxidation potentials. The oxidation potentials were determined by cyclic voltammetry using the standard calomel electrode (SCE) in dichloromethane (DCM). The HOMO level of TPD, *I*_D = 5.4 ± 0.1 eV, agrees well with the values reported previously, 5.4–5.5 eV.⁵ The lowest unoccupied molecular orbital (LUMO) levels (*A*_D, *A*_A) were estimated from Is and electronic absorption bands. Their values are within ±0.1 eV in agreement with those reported for TPD (Ref. 5) and bathocuproine (BCP),⁶ the latter corresponding to the BPT-based acceptors³ used in the present work. Experiments were performed with TPD:BPT[1:1](70 wt %):PC(30 wt %) and TPD:Gd(tmhd)₃BPT[1:1] blend films. The first one was spin coated from a 10 mg/ml dichloromethane solution onto precleaned ITO glass substrates and the second by vacuum coevaporation of TPD and Gd(tmhd)₃BPT compounds. The thickness of such prepared films ranged typically between 80

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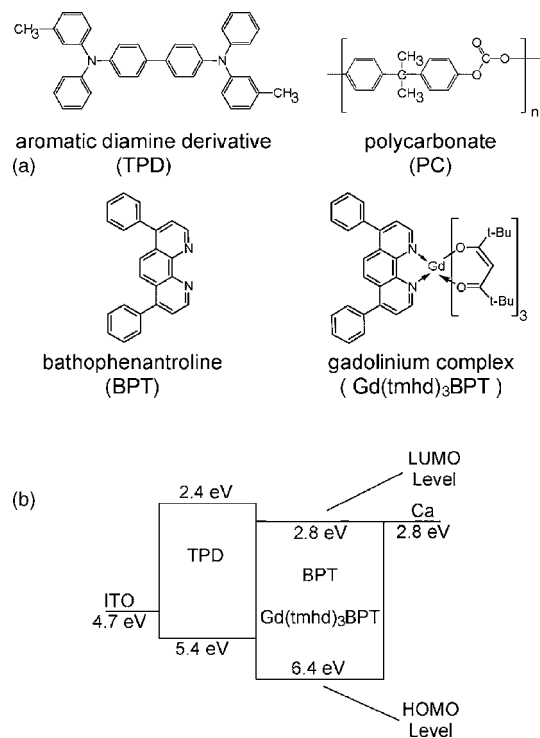
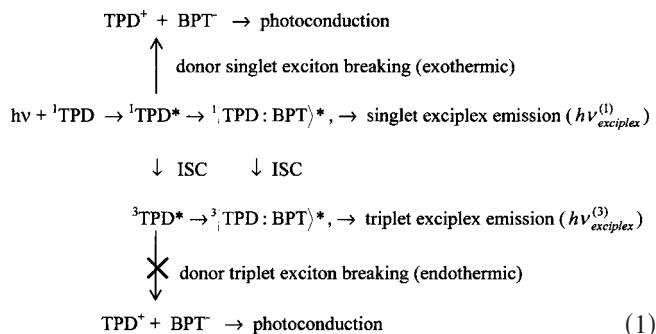


FIG. 1. Molecular structures (a) of the materials used in preparation of film emitters and energy level diagram (b) of the donor (TPD) and acceptor [BPT; Gd(tmhd)₃BPT] molecules forming emissive exciplexes. In addition to energy levels of the lowest unoccupied molecular orbitals (LUMO) and highest occupied molecular orbitals (HOMO) of organics, the Fermi level vacuum-referenced positions for ITO and Ca electrodes are given.

and 160 nm, except for a (1:1) Gd(tmhd)₃BPT:PC 2- μ m-thick film prepared by a precise doctor blade technique especially for the characterization of optical properties of the Gd(tmhd)₃BPT complex itself.

Figure 2 compares the absorption and PL spectra of single-component samples [Fig. 2(a)] and those for the donor (TPD):acceptor [BPT or Gd(tmhd)₃BPT] blends [Fig. 2(b)]. The PL spectra of the *D:A* systems are dominated by two different broadbands at $\lambda^{(1)} \cong 470$ nm and $\lambda^{(3)} \cong 570$ nm which have been shown to be characteristic of the emission from singlet $^1[\text{TPD}:\text{BPT}]^*$ and triplet $^3[\text{TPD}:\text{Gd}(\text{tmhd})_3\text{BPT}]^*$ exciplexes, respectively.³

The exciplex formation and emission, including photo-generation of charge, can be described by a sequence of the following processes:



$E_S \cong 3.0$ eV exceeds the electron-hole pair energy, $E_{\text{ch}} \cong (5.4-2.8)$ eV = 2.6 eV, by about $\Delta E_m = 0.4$ eV, while $\Delta E_{\text{exciplex}}^{(1)} = E_{\text{exciplex}}^{(1)} - E_{\text{ch}} = (2.64-2.6)$ eV = 0.04 eV and $\Delta E_{\text{exciplex}}^{(3)} = E_{\text{exciplex}}^{(3)} - E_{\text{ch}} = (2.18-2.6)$ eV = -0.42 eV (endot-

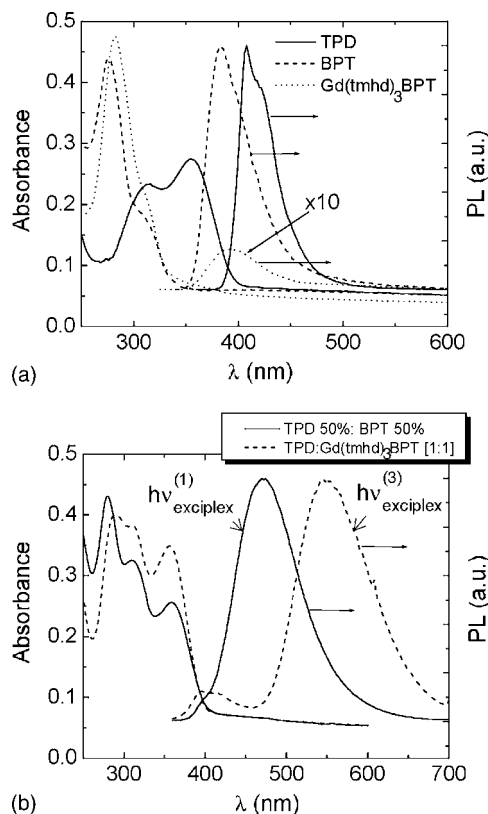


FIG. 2. Absorption and emission spectra of (70 \pm 10)-nm-thick (a) single-active component films of TPD(40%):PC(60%) (solid lines), BPT(40%):PC(60%) (dashed lines), and Gd(tmhd)₃BPT (100%) (dotted lines) and (b) their blends as described in the text. Here and throughout all the work, the PL has been excited at $\lambda_{\text{exc}} = 350$ nm.

hermic). The effect of the $^3\text{TPD}^*$ molecular triplets breakdown on the PL decay and its contribution to the photocurrent can also be neglected on the ground of energetics. Their energy, $E_T = 2.3$ eV,⁶ makes it an endothermic process requiring an activation over a 0.3 eV barrier. Finally, singlet-singlet, singlet-triplet, and triplet-triplet annihilation processes are not expected to affect the PL outcome as the excitation light intensity in all experiments carried out in this study did not exceed $I_{\text{exc}} = 10^{15}$ photons/cm² s. The mutual annihilation effect of excited states on the PL efficiency is usually observed at $I_{\text{exc}} > 10^{17}$ photons/cm² s.^{7,8}

The charge photogeneration is characterized directly by the photocurrent (*j*) plots versus applied electric field (*F*) in Fig. 3. The corresponding exciplex emission quenching is shown in Fig. 4. From Fig. 3 we learn that the photocurrent (*j*) largely exceeds the dark current (*j*_{dark}) either for the forward (ITO⁺, Ca⁻) (*j*₊) or the reverse (ITO⁻, Ca⁺) (*j*₋) biased cell. This indicates the current to be produced in the sample volume. Figure 4 shows the electric field dependence of the PL quenching defined as $\delta = [\Phi_0 - \Phi(F)]/\Phi_0$, where $\Phi(F)$ is the PL output at a field *F* and Φ_0 is the PL output at *F* = 0. Some differences apparent within the low-field region (*F* < 0.75 MV/cm) for the two acceptors and opposite polarizations of the ITO anode practically disappear at high fields. This indicates that the high-field quenching belongs to an electric-field-imposed reduction in the final exciplex emission yield based on a common physical mechanism for all the samples and both polarizations of electrodes.

We propose that the principal PL quenching mechanism is due to the interaction between donor singlet excitons and acceptor-localized electrons,

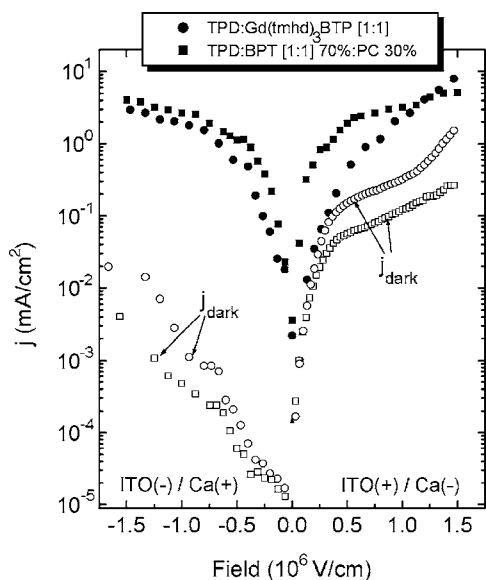


FIG. 3. Photocurrent j (filled figures), and dark current j_{dark} (open figures) as functions of applied field with the injection forward ITO(+) and reversed ITO(-) electrode bias for the phosphorescent TPD:Gd(tmhd)₃BTP and fluorescent TPD:BPT blend films.



The concentration of excited donor singlets (S_0) decreases in external electric field (S) because of increasing concentration (n) of electronic charge and because their breaking rate increases: $\delta(F) = \Delta S/S_0 = (S_0 - S)/S_0 = 1 - (\gamma_{\text{Sq}} n \tau)^{-1}$. Here, γ_{Sq} is the exciton-charge carrier interaction rate constant, τ is the exciton intrinsic lifetime, and $n = \eta I_{\text{exc}} / \mu F$ which is in general a complex function of electric field since the quantum efficiency of charge separation (η) and carrier mobility (μ)

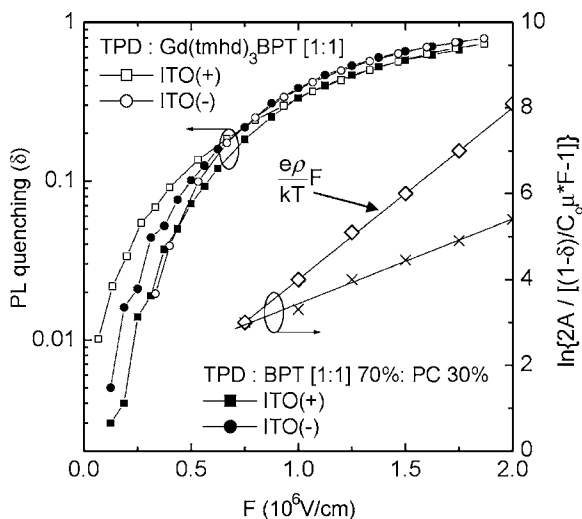


FIG. 4. Left-hand ordinate: the PL quenching (δ) as a function of applied electric field (F) for two different composition films and electrical bias electrodes as described in the figure. Right-hand ordinate: the high-field range (from $F_i = 0.75 - 2$ MV/cm) $\ln[2A / [(1 - \delta) / C_0 \mu^* F - 1]] = e\rho F / kT$ vs F plots extracted according to Eq. (3) from the experimental values of δ (left-hand ordinate) for two limiting cases, $\mu^*(F) = \text{const}$ (crosses) and $\mu^* = \mu / \mu_i = \exp[\beta_\mu (F^{1/2} - F_i^{1/2})]$ (diamonds), where β_μ is the factor scaling the Poole-Frenkel-type field dependence of the mobility (μ)². Its best fit (diamonds) to the straight-line plot of $e\rho F / kT$ (solid line) is obtained with $e\rho / kT = 4 \times 10^{-6}$ cm/V ($\rho = 1$ nm, $kT = 0.025$ eV), $A = 10^4$, $C_0 = 1.1 \times 10^{-9}$ cm/V, and a field dependent μ^* with $\beta_\mu \cong 4.6 \times 10^{-3}$ (cm/V)^{1/2}.

are field dependent quantities.² Due to the exothermic nature of the ${}^1\text{TPD}^*$ dissociation, the effect of electric field on hopping rate of the initially separated carriers seems to be the most suitable model to describe the present results. The quantum efficiency of charge separation in this model is given by⁹ $\eta(F) = \sinh(e\rho F / kT) / [A + \sinh(e\rho F / kT)]$, where $A = (k_r + k_n) / k_0$ is the ratio of the overall decay [radiative (k_r) and nonradiative (k_n)] rate constant of the exciton and k_0 is the zero-field value of the rate constant for the formation of a $\text{TPD}^+ - \text{BPT}^-$ pair, $k_{\text{ch}}(F) = k_0 \exp(e\rho F / kT)$, and ρ is the hopping distance of a quenching active carrier.

Within this model, the PL high-field quenching signal can be expressed as

$$\delta = 1 - \frac{\mu F}{\gamma_{\text{Sq}} \tau I_{\text{exc}}} [1 + 2A \exp(-e\rho F / kT)]. \quad (3)$$

We note that Eq. (3) imposes an excitation-dependent upper limit on electric field values, $F < (kT / e\rho) \ln(2A)$. Its meaning comes from the above definition of n , assuming the volume generation-controlled current. Rewriting Eq. (3) in the form $\ln[2A / [(1 - \delta) / C_0 \mu^* F - 1]] = e\rho F / kT$ allows its straightforward comparison with the experimental data as shown in Fig. 4. The value of the fitting parameter A indicates that the zero-field value of the e-h formation rate constant is roughly four orders of magnitude smaller than other, mostly nonradiative, decay rate constants of molecular TPD excitons and limits the applicability of the model for high fields but below 2.5×10^6 V/cm. This limit could be increased for $\rho < 1$ nm and $A > 10^4$.

In conclusion, we suggest a model explaining the observed strong electric field quenching effect on the exciplex-underlain emission from electron donor (D)-electron acceptor (A) blends ($D:A$) exemplified by the fluorescent TPD:BPT and phosphorescent TPD:Gd(tmhd)₃BTP systems. We show that the field-induced reduction of the emission in both cases reflects the common quenching mechanism due to the donor molecular singlet exciton interaction with electrons localized on and transported by acceptor molecules. The large quenching signals are ascribed to the high concentration of charge produced efficiently by the field-enhanced electron-hole separation between $D-A$ molecules and making the system highly photoconductive.

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