



Fluorescence and phosphorescence behavior of TPD doped and TPD neat films

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ABSTRACT

Photoluminescence spectra of N,N'-bis(3-methylphenyl)-N,N'-bis(phenyl)-benzidine (TPD) are studied in a temperature range from 10 K to room temperature using a neat TPD film, and 5 wt.% TPD doped films with polystyrene (PS), 4,4'-N,N'-dicarbazole-biphenyl (CBP), and polycarbonate (PC) as hosts. The photo-excitation occurred in the singlet absorption region of TPD. The blue fluorescence and green phosphorescence quantum yields, ϕ_F and ϕ_P , of TPD are determined from their quantum distributions, $E_F(\lambda)$ and $E_P(\lambda)$. The yields are found to be $\phi_F = 0.39$ and $\phi_P = 0.012$ for neat films at room temperature, while $\phi_F = 0.78$ and $\phi_P = 0.026$ are measured for a TPD doped PS film. The lower luminescence quantum yield in the neat film is caused by self-quenching.

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1. Introduction

Thin films of the aromatic diamine molecule N,N'-diphenyl-bis(3-methylphenyl)-biphenyl-4,4'-diamine (abbreviated by TPD) are widely used as hole-transport layer in organic light emitting diodes (OLEDs) because of high hole mobility ($\mu_h \approx 1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature) and low electron mobility ($\mu_e/\mu_h < 10^{-5}$) [1,2]. TPD is also used as a host material for phosphorescent guest molecules in OLED devices like PtOEP and Ir(ppy)₃ [3,4].

The fluorescence behavior of TPD was studied in [2,5–7]. Fluorescence quantum yields of $\phi_F = 0.35$ [2,5] and 0.40 [6] have been reported for TPD neat films. A fluorescence quantum yield of $\phi_F = 0.69$ was obtained for TPD dissolved in the liquid solvent 1,4-dioxane [6]. For 4 wt.% TPD doped into polystyrene a fluorescence quantum yield of $\phi_F \approx 0.6$ was measured [7].

Here we study in a range from 10 K to room temperature the photoluminescence (PL) behavior of (i) a neat thin film of TPD, and (ii) of thin films with 5 wt.% TPD as guest in the hosts polystyrene (PS), 4,4'-N,N'-dicarbazole-biphenyl (CBP), and bisphenol-A-polycarbonate (PC). Luminescence quantum distributions and luminescence quantum yields are determined.

2. Experimental procedures

The thin films were prepared by spin-coating the appropriate solutions on optical glass substrates under ambient atmospheric conditions. The neat TPD film was prepared by spin-coating a

solution of 20 mg TPD per 1 ml THF onto a microscope glass carrier plate at a speed of rotation of 1200 rpm. The obtained film thickness was $d_f = 67 \text{ nm}$, as determined by transmission measurements.

For the spin-coating of 5 wt.% of TPD in PC, solutions of 2 mg TPD in 0.5 ml dichloromethane and 38 mg PC in 0.5 ml dichloromethane were mixed together and dropped on the plate spinning with a speed of 450 rpm (obtained film thickness $d_f = 231 \text{ nm}$). 5 wt.% TPD in CBP was prepared by mixing 0.5 mg TPD in 0.5 ml THF with 9.5 mg CBP in 0.5 ml THF and spin-coating the solution with a speed of 900 rpm (obtained film thickness $d_f = 223 \text{ nm}$). The films containing 5 wt.% TPD in polystyrene were prepared by mixing 1 mg TPD in 0.5 ml THF and 19 mg PS of different molar mass (weight-average molar mass $M_w = 2000, 20,000, 100,000,$ and $500,000 \text{ g mol}^{-1}$) in 0.5 ml THF and spin-coating the solutions at 1200 rpm.

Absolute intrinsic luminescence (i.e., fluorescence and phosphorescence) quantum distributions, $E_L(\lambda)$, were measured at room temperature with a self-assembled fluorimeter in front-face collection arrangement [8,9] (for the definition of intrinsic luminescence quantum distribution see [10]). The experimental setup is described in [11]. The samples were excited with a 200 W high-pressure mercury lamp. The excitation wavelengths were selected with interference filters. The samples were excited with vertically polarized light and the luminescence was collected under magic angle conditions (polarizer in luminescence path oriented under an angle of 54.7° to the vertical). For absolute quantum yield calibration the dye quinine sulfate dihydrate (from Aldrich) dissolved in 1 normal aqueous H_2SO_4 (fluorescence quantum yield $\phi_F(C) = 0.546$ [12]) was used as reference. The luminescence quantum yield is given by $\phi_L = \int E_L(\lambda) d\lambda$ where the integral extends over the full emission wavelength region.

PL spectra were measured at various temperatures between 10 K and 290 K with a Spex-Fluorolog-3 fluorophotometer. The excitation

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source was a 450 W Xe lamp. Corrections were made for the spectral sensitivity of the detection system.

3. Results and discussion

3.1. Luminescence quantum distributions and quantum yields

Fig. 1 shows photoluminescence quantum distributions of TPD from a film of PS ($M_w = 100,000 \text{ g mol}^{-1}$) doped with 5 wt.% TPD which was excited at 330 nm. The most intense and the second most intense peak are observed at 397.2 nm and 418.8 nm, respectively, and a shoulder is present at 440 nm. The band structure is attributed to vibronic $S_1(0) \rightarrow S_0(v)$ fluorescence emission of TPD (v indicates vibrational quantum number). A structured weak emission is observed in the long-wavelength emission tail with peaks at 522.1 nm, 556 nm and a shoulder at 600 nm. This emission is attributed to vibronic $T_1(0) \rightarrow S_0(v)$ phosphorescence. It is noted that the T_1 emission is observed even at high temperature like room temperature. The luminescence quantum yield, ϕ_L , decreases somewhat with decreasing temperature. Similar spectra were obtained for CBP and PC films doped with 5 wt.% TPD and for the neat TPD film.

The luminescence quantum distribution, $E_L(\lambda)$, is the sum of the fluorescence quantum distribution, $E_F(\lambda)$, and the phosphorescence quantum distribution, $E_P(\lambda)$, i.e., $E_L(\lambda) = E_F(\lambda) + E_P(\lambda)$. For TPD below 480 nm the luminescence emission is fully due to fluorescence emission. Above 480 nm the fluorescence emission and the phosphorescence emission overlap. The spectra may be separated by assuming a linear extension of the slope in the logarithmic presentation of the fluorescence spectra in the long-wavelength region. With this approximation the long-wavelength fluorescence quantum distribution is given by $E_F(\lambda) = E_F(\lambda_0) \exp[-(\lambda - \lambda_0) / \delta\lambda]$ ($\lambda_0 = 480 \text{ nm}$, $\delta\lambda$ is slope of fluorescence tail). An example of the separation of a luminescence spectrum in its fluorescence contribution and phosphorescence contribution is shown in Fig. 2 for 5 wt.% TPD in CBP at 10 K.

Phosphorescence quantum yields, $\phi_P = \int E_P(\lambda) d\lambda$, were estimated from the separated phosphorescence quantum distributions, $E_P(\lambda)$. These phosphorescence quantum yields give the ratio of the intrinsic number of photons emitted by $T_1 \rightarrow S_0$ radiative transition to the number of absorbed photons. The absorption occurred in the singlet state absorption region since we used excitation with 330 nm or 360 nm UV light. Therefore ϕ_P is phosphorescence quantum yield induced by the singlet photon absorption. In Table 1 the quantum yields ϕ_L , ϕ_P , and ϕ_F obtained at room temperature are listed.

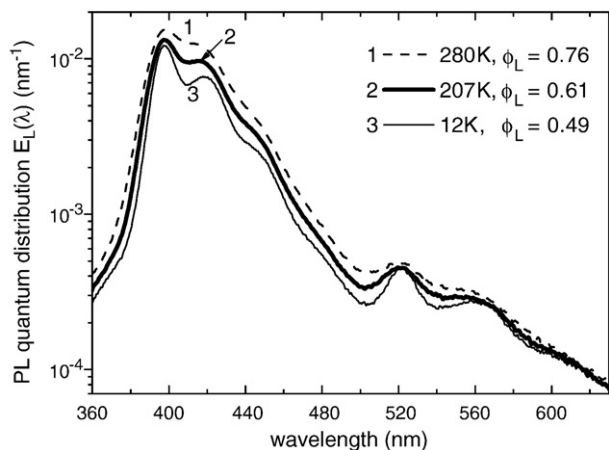


Fig. 1. Photoluminescence quantum distribution, $E_L(\lambda)$, of 5 wt.% TPD doped PS film at three temperatures. Weight-average molar mass of PS is $M_w = 100,000 \text{ g mol}^{-1}$. Excitation wavelength $\lambda_{exc} = 330 \text{ nm}$.

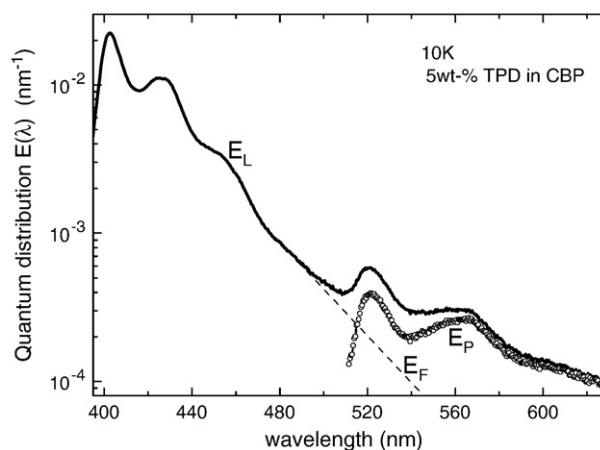


Fig. 2. Photoluminescence quantum distribution, $E_L(\lambda)$, of 5 wt.% TPD doped CBP film at 10 K. $\lambda_{exc} = 360 \text{ nm}$. The broken line shows the expected long-wavelength fluorescence contribution. The line with circles shows the extracted phosphorescence contribution.

In the PS films, the fluorescence and phosphorescence quantum yields of TPD increase with increasing weight-average molar mass M_w of PS. A maximum value of $\phi_F \approx 0.78$ was obtained for PS with $M_w = 500,000 \text{ g mol}^{-1}$. This value is almost the same as obtained for TPD in CBP ($\phi_F = 0.795$) and PC ($\phi_F = 0.76$) hosts. For TPD in 1,4-dioxane a fluorescence quantum yield of $\phi_F = 0.69$ was measured [6]. The high fluorescence quantum yields of the TPD guest molecules in solid hosts make them good blue emitters in OLED devices.

3.2. Luminescence loss processes

We determined a luminescence quantum yield of $\phi_L = 0.40$ for a spin-coated neat TPD film (see also [6]). This is consistent with the results of Mattoussi et al. [4] and Garbuzov et al. [5] who determined $\phi_L = 0.35 \pm 0.03$ (their films were prepared by vacuum vapor deposition on SiO_2 glass substrates). The neat film luminescence quantum yields are smaller than the luminescence quantum yields of 5 wt.% TPD doped films with luminescence quantum yields between 61% (TPD in PS with $M_w = 2000 \text{ g mol}^{-1}$) and 81% (TPD in CBP, see Table 1).

In neat TPD films the luminescence is dominantly reduced by self-quenching because of a much stronger overlap between the absorption and emission spectra than in the doped film. Additionally excitation migrates very fast by Förster-type energy transfer to quenching centers in neat films [11]. Excitation migration also occurs by exchange interaction (Dexter-type energy transfer) since the TPD molecules are in contact (electronic wave-functions overlap). Electron transfer between excited TPD molecules and adjacent ground-state TPD molecules takes place with electron back-transfer (no excitation loss) and non-radiative charge recombination (excitation loss) according to $\text{TPD} + \text{TPD} + h\nu \rightarrow \text{TPD}^* + \text{TPD} \rightleftharpoons \text{TPD}^+ + \text{TPD}^- \rightarrow \text{TPD} + \text{TPD}$. These processes occur in the neat film resulting in low quantum yield.

In lightly doped TPD films the luminescence reduction is caused by the non-radiative processes of internal conversion and intersystem crossing [10,13,14]. At a doping level of 5 wt.% concentration quenching already reduces the luminescence efficiency [2]. There occurs already dipolar (Förster-type) excitation migration [10] to quenching centers where the excitation is lost by non-radiative processes. The T_1 energy level of TPD is at $\approx 2.44 \text{ eV}$ (estimated from Fig. 2), while the T_1 energy levels of the hosts are higher at 2.58 eV for CBP [7,15], 2.9 eV for PC [16], and 3.3 eV for PS [7,15]. This hinders loss of TPD phosphorescence by triplet excitation transfer from the TPD guest to the CBP, PC, and PS hosts.

When TPD is doped with phosphorescent PtOEP and excitation occurs in the singlet absorption region of both TPD and PtOEP, then the TPD fluorescence emission in the violet/blue/green spectral region

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