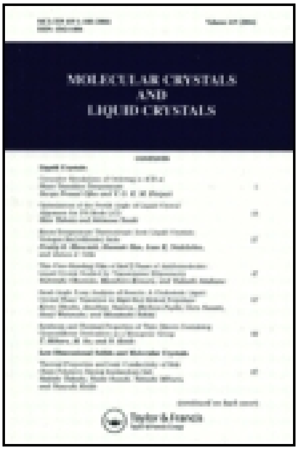

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The Influence of Polymer Matrix Parameters on Intersystem Crossing in Dopant Molecules of Aromatic Amines

Yu. A. Skryshevski [a] & A. Yu. Vakhnin [a]

[a] Institute of Physics (NASU), Kyiv, Ukraine

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The Influence of Polymer Matrix Parameters on Intersystem Crossing in Dopant Molecules of Aromatic Amines

Yu. A. Skryshevski
A. Yu. Vakhnin
Institute of Physics (NASU), Kyiv, Ukraine

The luminescence spectra of carbazole and phenyl-substituted amines in toluene solution and wide set of polymer matrix were studied at 5 and 295 K, as well as their parameters were obtained. The intersystem crossing was shown to be important process influencing on the energy relaxation of excited singlet state. Its efficiency depends not only on the chemical nature of substituents and spatial conformation of molecule, but also is conditioned by interaction with ambient medium. Therefore, the rate of intersystem conversion increases upon influence of external heavy atom, and also when the polymer matrix is changed or pressure up to 3 kbar is applied.

Keywords: aromatic amines; fluorescence; intersystem crossing; phosphorescence; polymer matrix

INTRODUCTION

The films of polystyrene (PS) and polycarbonate (PC) doped with great concentration ($C \approx 1\,\mathrm{M}$) of aromatic amine are widely used as hole transport layers in electrophotographic receptors for coppiers and laser printers [1]. The vacuum-deposited layers of the same molecules, as well as amorphous films of special polymers, which macromolecules are chemically modified by introducing as fragments the phenyl-substituted amines in order to combine both transport and light-emitting properties within the single layer, are utilized in organic electroluminescent diodes (OLEDs)

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Address correspondence to Yu. A. Skryshevski, Institute of Physics (Nasu), 46, Nauki Ave., Kyiv-28, Ukraine. Tel.: 380-44-265-30-14, Fax: 380-44-265-15-89, E-mail: skrysh@iop.kiev.ua

[2,3]. So, the substituted amines, which phenyl fragments are modified by adding of methyl and/or methoxy groups for preventing the molecules from crystallization in film, are preferably used in devices [1].

During xerographic process the surface of photoreceptors is charged by corona discharge in the air, which is accompanied by UV-irradiation together with production of singlet oxygen, ozone and nitric oxides [1,4]. As a result, a variety of photochemical reactions occurs, in particular the photocyclization of phenyl-substituted amine into the carbazole. As a rule, this reaction proceeds when initial molecule is in the excited triplet T_1 state [5,6]. Besides, the intersystem crossing from singlet S_1 to the T_1 state is of great significance for relaxation of excited molecule itself [7,8]. Although the S_1–T_1 crossing, as well as radiative and radiationless transitions from T_1 into ground S_0 state, are spin-forbidden, they all are partly resolved due to spin-orbital interaction, which mixes singlet and triplet states of molecule. In addition, the probability of these transitions is conditioned by chemical and conformational features of molecule, and as well by interaction with ambient medium [7,9,10].

Till now, the spectral luminescence properties of aniline, diphenylamine (DPA) and their methyl substituted derivatives, triphenylamine (TPA), as well as amine-substituted aromatic polycyclic hydrocarbons, have been studied in details [see, for example, 5,9–11]. But the spectra of aromatic amines of more complicated structure were not perfectly investigated [4,6]. The present work establishes the interrelation between the chemical structure of phenyl-substituted amines, which phenyl fragments are bound with methyl and methoxy groups, and their luminescence properties in solution and polymer matrix at the temperature $T = 5$ and 295 K. For this purpose, the fluorescence (Fl) and phosphorescence (Ph) spectra of toluene solutions were studied, as well as the Fl quantum yield (Φ_{Fl}) and Ph decay time (T_{Ph}) were determined, for the following compounds: carbazole (Cz), DPA, TPA, tri-*p*-tolylamine (TTA), di-*p*-tolylamine-*p*-anisylamine (DTA), di-*p*-anisylamine-*p*-tolylamine (DAT), tri-*p*-anisylamine (TAA), N,N′-diaminobiphenyl (N,N′-DABP) and N,N′-diphenyl-N,N′-bis(3-methylphenyl)-1,1′-bipheny-4,4′-diamine (TPD). The structure formulae of molecules are presented in Figure 1. To ascertain a relation of the efficiency of intersystem S_1–T_1 and T_1–S_0 transitions vs polymer matrix density (ρ), the luminescence properties (both Fl and Ph, at $T = 5$ and 295 K) of TTA an TPD in polyethylene (PEt), polystyrene (PS), poly(4-bromo)styrene (4BrPS), polycarbonate (PC) and polyvinylenechloride (PVCl) were investigated as for usual conditions, and also under applying of uniaxial pressure of 3 kbar for TTA and TPD in PS, 4BrPS and PC matrices.

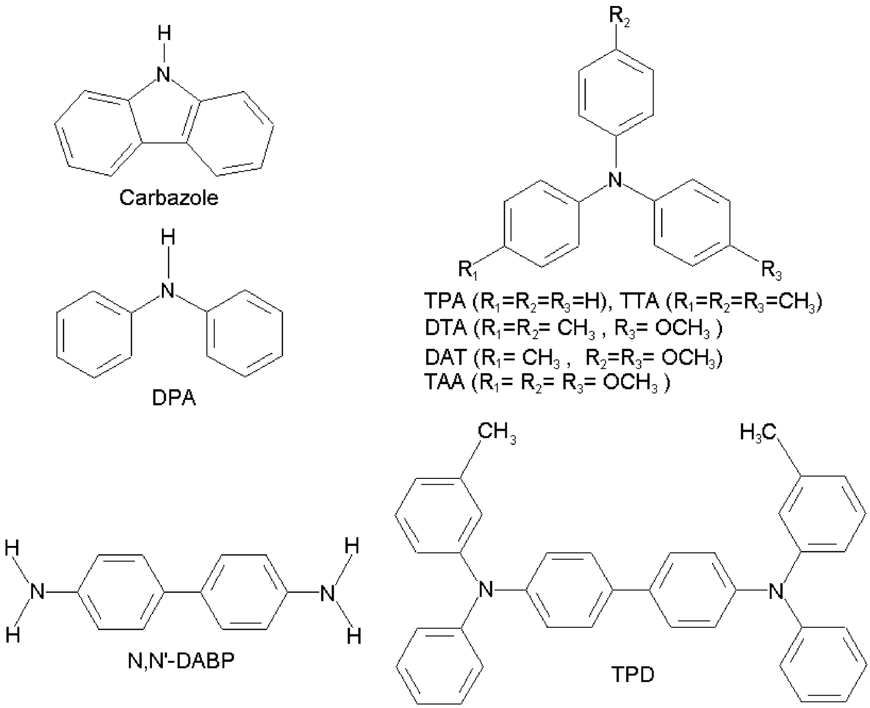

FIGURE 1 Structure formulae of molecules of carbazole and phenyl-substituted amines.

EXPERIMENTAL

The doped films of PS, 4BrPS and PC with thickness up to 10 microns were fabricated on quartz substrates by casting of toluene solution of polymer, which was previously mixed with solution of proper aromatic amine. The samples were dried at room temperature. Since PEt and PVCl are both insoluble in common solvents, the films of specified polymers were wetted in toluene solution of TTA or TPD for several hours at $T = 370\,\text{K}$. The luminescence signal was excited by filtered radiation of high-pressure Hg-lamp (250 W) at $\lambda_{\text{ex}} = 313\,\text{nm}$ and measured by double-grating spectrometer SDL-1. During all measurements the samples were placed in the helium atmosphere inside temperature operated optical cryostat. For measurement of T_{Ph} the record of Ph signal was made after cutting off the *cw* light of Hg-lamp by mechanical shuttle. For density variation, when one and the same polymer was used, the uniaxial squeezing was created by screw micropress with sapphire window.

The pressure magnitude up to 3 kbar was measured by shift of the 694.2 nm luminescence line of ruby microcrystall.

RESULTS AND DISCUSSION

Let us consider a relationship between the chemical structure of amine molecules and their luminescence properties in liquid and frozen toluene solution ($C = 10^{-5}$ M). The Fl spectrum of carbazole at $T = 295$ K was shown to have distinct vibronic structure (Fig. 2 curve *1*) and agreed well with proper spectrum in ethanol solution [11]. Unlike carbazole, the Fl spectra of DPA, TPA, TTA, DTA, DAT, TAA, N,N′-DABP and TPD consist of wide and structureless band and comply with published ones for solutions of DPA, TPA, TTA, N,N′-DABP in cyclohexane or ethanol [11,12].

The Fl spectra of toluene solutions of DPA and TPD are depicted in Figure 2 (curves *2* and *3*) for example, while the positions of Fl band maximum (λ_m^{Fl}) of foregoing amines and carbazole are given in Table 1. The fluorescence yield of oxygen-free solution of TPA in toluene at $T = 295\,K = 0.05$ [8].

Using this magnitude as reference one, appropriate values for other studied amines in the same solvent were calculated (see Table). It was also ascertained that change of the toluene by the solid matrix like PS does not effect on Φ_{Fl} within the 10% of its value for all molecules under study.

The luminescence spectra of frozen toluene solutions of TPA, TTA, DTA, DAT, TAA and TPD ($T = 5$ K) are represented in Figure 3. The

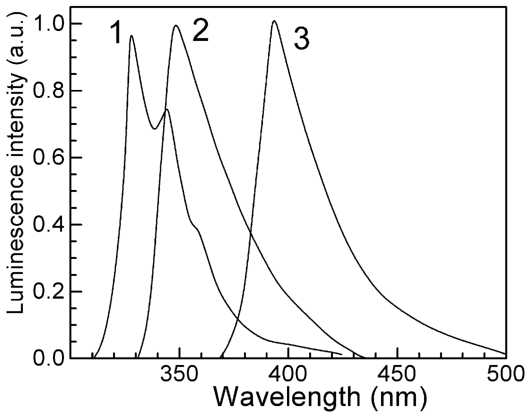

FIGURE 2 Fluorescence spectra of toluene solutions ($C = 10^{-5}$ M) of carbazole (*1*), DPA (*2*) and TPD (*3*) at $T = 295$ K.

TABLE 1 Luminescence Parameters of Solutions of Carbazole and Phenyl-Substituted Amines in Toluene

	$T = 295\,\mathrm{K}$		$T = 5\,\mathrm{K}$				
Molecule	λ_m^{Fl}, nm	Φ_{Fl}	λ_m^{Fl}, nm	λ_m^{Ph}, nm	E_m^{Fl}–E_m^{Ph}, eV	Φ_{Ph}/Φ_{Fl}	T_{Ph}, s
Carbazole	340	0.38	335	395	0.56	1	5
DPA	350	0.08	345	398	0.48	3	2
TPA	360	0.05	355	408	0.45	7	0.8
TTA	370	0.05	370	417	0.38	7	0.8
DTA	375	0.05	375	422	0.37	7	0.8
DAT	385	0.05	385	430	0.34	7	0.8
TAA	390	0.05	390	435	0.33	7	0.8
N,N′-DABP	375	0.26	380	510	0.83	0.1	0.7
TPD	395	0.27	400	520	0.72	0.1	1.3

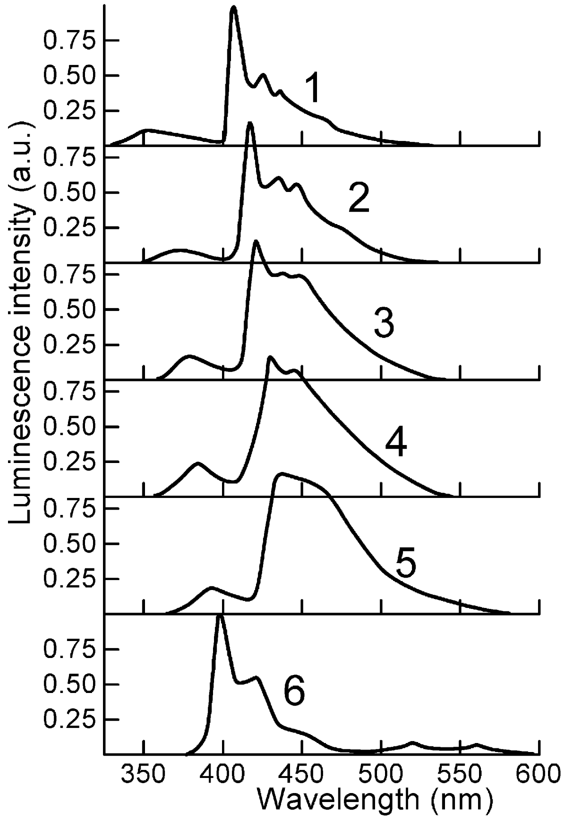

FIGURE 3 Luminescence spectra of solutions ($C = 10^{-5}\,\mathrm{M}$) of TPA (*1*), TTA (*2*), DTA (*3*), DAT (*4*), TAA (*5*) and TPD (*6*) in toluene at $T = 5\,\mathrm{K}$.

proper values of λ_m^{Fl}, maximum position of Ph spectra (λ_m^{Ph}), the difference between these values in energy units (E_m^{Fl}–E_m^{Ph}) together with ratio of quantum yields of respective emission spectra (Φ_{Ph}/Φ_{Fl}), and also T_{Ph} for the frozen solutions of these amines and carbazole are given in Table. It is found that under cooling of the doped PS films down to 5 K the value of Φ_{Fl} increases by 15–20%.

As it follows from data of Table, within series TPA, TTA, DTA, DAT and TAA a continuous bathochromic shift of emission band positions λ_m^{Fl} and λ_m^{Ph}, as well as (E_m^{Fl}–E_m^{Ph}) value lowering, are observed by analogy with spectral variations within linear polyacens series [9,10]. When TPA is changed for TTA, such spectral behaviour is likely caused by partial conjugation of σ-electron of methyl substituent carbon atom with π-electron system of adjacent phenyl ring for TTA. In turn, these spectral changes are more pronounced under the consecutive substitution of methyl groups by electron-donating methoxy ones within the set TTA, DTA, DAT, TAA, and are originated by conjugation of unshared electron pair of oxygen heteroatom with π-electrons of neighboring phenyl fragment. The bathochromic shift of Fl spectrum upon replacing the benzene by xylole and anisole [11] was explained in the similar way [10]. A vibronic structure is nearly absent in Fl spectra of solutions of DPA, TPA, TTA, DTA, DAT, TAA at $T = 5$–295 K and TPD at $T = 295$ K, that is apparently caused by inhomogeneous broadening as a consequence of unrigid molecule structure. This explanation is argued by noticeable vibronic structure in Fl spectrum of carbazole and lack of it for DPA, whereas both molecules contain eight π-electrons, but the first one is planar and rigid, while the second one has solid and unrigid skeleton [10]. As it takes place for majority of substituted amines, the Fl spectrum of frozen solution of N,N′-DABP is structureless, unlike that of TPD (Fig. 3, curve *6*). This evidences in favour of more ordered conformation of TPD molecule at low temperature due to steric constraints. Figure 3 (curves *1–5*) shows that Ph spectra of TPA and TTA have a clearly expressed vibronic structure, that is gradually smoothed for DTA, DAT, TAA. This situation is probably caused by inhomogeneous broadening owing to presence of the set of isomers of these molecules as a result of methoxy group turning relative to phenyl ring plane.

As one can see from Table, the molecules of DPA, TPA, TTA, DTA, DAT, TAA have a very low value of Φ_{Fl}. In the Ref. [8] there was shown that at low temperature the principal mechanism of radiationless deactivation of S_1 state for composite aromatic molecules, including DPA and TPA, is intersystem crossing, and quantum yield of this process for TPA is close to unit. The probabilities of S_1–T_1 and T_1–S_0 transitions are known [7,9] to depend directly on the strength of spin-orbital interaction and energy difference of S_1 and T_1 states. The stereoconformation of molecules DPA, TPA, TTA, DTA, DAT and TAA has the $2p_Z$-orbital of unbound electron pair of nitrogen heteroatom to be inclined with respect to the $2p_\pi$-orbitals of phenyl ring, unlike the carbazole molecule, that is characterized by the $2p_Z$-orbital of heteroatom to be oriented in parallel to the $2p_\pi$-orbitals of π-system. So, the probability of intersystem crossing (both S_1–T_1 and T_1–S_0) for this set of molecules must be higher than for carbazole [10]. When we are going on from carbazole to the set of DPA, TPA, TTA, DTA, DAT and TAA (see Table), the value of E_m^{Fl}–E_m^{Ph}, the magnitudes of Φ_{Fl} and T_{Ph} decrease, while the ratio Φ_{Ph}/Φ_{Fl} rises. This tendency is explained by strengthening of spin-orbital interaction because of non-planar molecular conformation. For N,N′-DABP and TPD molecules a general correlation between above parameters is saved: the ratio Φ_{Ph}/Φ_{Fl} decreases, while the values of (E_m^{Fl}–E_m^{Ph}), T_{Ph} and Φ_{Fl} increase. Therefore, the higher magnitude of Φ_{Fl} for the last case is predominantly conditioned by the lowering of the probability of S_1–T_1 intersystem crossing because of increase in energy separation between S_1 and T_1 levels.

The luminescence spectra at $T = 5\,K$ of TTA-doped polymers ($C = 10^{-5}$ M) are depicted in Figure 4 for PEt and PVCl matrices, in Figure 5 for PS and 4BrPS ones. The similar spectra for PS, PC and 4BrPS doped by TPD ($C = 10^{-5}$ M) are presented in Figure 6. As compared with frozen toluene solutions, the spectra of doped polymers have smoothed vibronic structure and relatively more intense

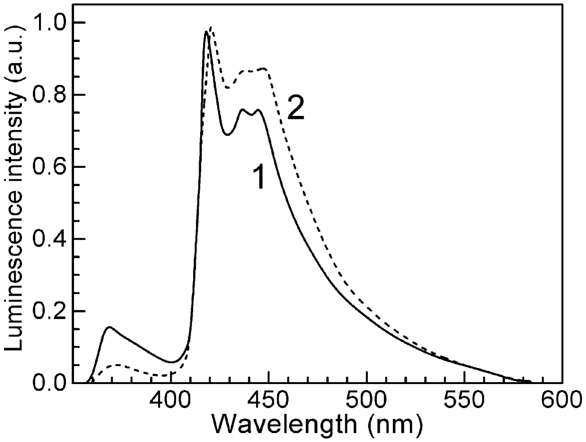

FIGURE 4 Luminescence spectra at $T = 5$ K of TTA ($C = 10^{-5}$ M) in PEt (*1*) and PVCl (*2*).

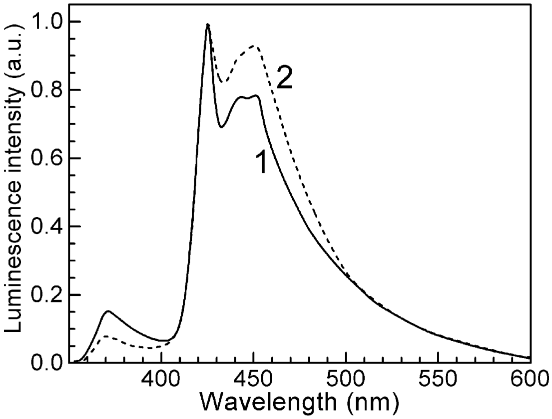

FIGURE 5 Luminescence spectra at $T = 5\,\mathrm{K}$ of TTA ($C = 10^{-5}$ M) in PS (*1*) and 4BrPS (*2*).

phosphorescence, i.e., greater ratio $\Phi_{\mathrm{Ph}}/\Phi_{\mathrm{Fl}}$, while $\mathrm{T_{Ph}}$ remains nearly unchanged. These features become gradually more pronounced within this set of polymers and correlate good with the rise of matrix density (for PEt, PS, PC, PVCl series a density equals 0.92, 1.05, 1.2 and $1.4\,\mathrm{g/cm^3}$, respectively). For example, when PVCl is used instead of PEt for TTA, and PC instead of PS for TPD, the ratio $\Phi_{\mathrm{Ph}}/\Phi_{\mathrm{Fl}}$ nearly doubles. At the same time, the changes in luminescence properties for all studied amines in 4BrPS, as compared with those ones in PS,

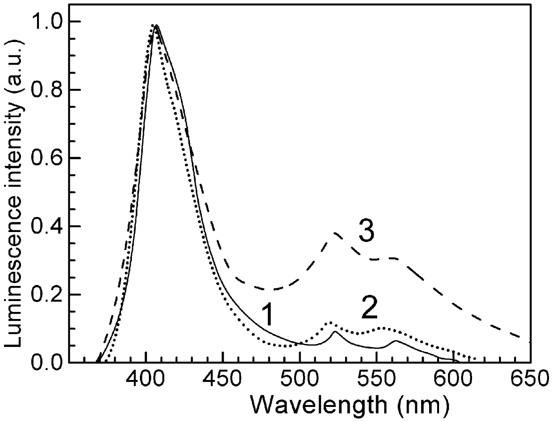

FIGURE 6 Luminescence spectra at $T = 5\,\mathrm{K}$ of TPD ($C = 10^{-5}$ M) in PS (*1*), PC (*2*) and 4BrPS (*3*).

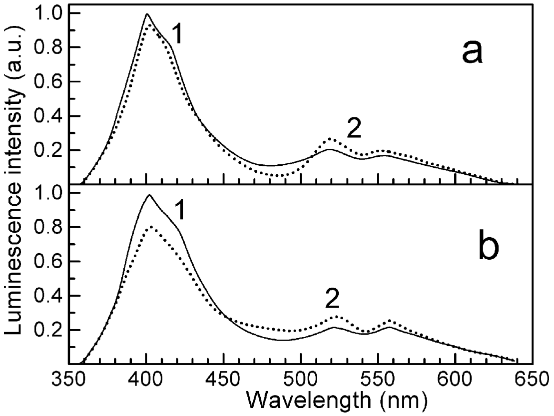

FIGURE 7 Luminescence spectra at $T = 5\,\mathrm{K}$ of TPD ($C = 10^{-3}$ M) in PS (a), and 4BrPS (b) without (*1*) and under application of pressure of 3 kbar (*2*).

consist in significant decrease in the Φ_{Fl} and T_{Ph} values (nearly twice) accompanied by increase in Ph yield Φ_{Ph}, that results in considerable growth of the ratio $\Phi_{\mathrm{Ph}}/\Phi_{\mathrm{Fl}}$ by a factor of $2.0 \div 3.0$ (Figs. 5 and 6, curves *1* and *3*). The last features can be unambiguously explained by increase in probabilities (and rates) of both S_1–T_1 and T_1–S_0 crossing owing to influence of external heavy atom [7,9], that is exactly a consequence of mixing of electron wave functions of π-system of amine and outer orbital of bromine.

The luminescence spectra at $T = 5\,\mathrm{K}$ of TPD in matrices of PS and 4BrPS ($C = 10^{-3}$M), which were measured immediately before and after applying the uniaxial pressure of 3 kbar to polymer film, are depicted in Figure 7. Under pressure, the spectral position of luminescence bands and the value of T_{Ph} remain unchanged, while the phosphorescence intensity (and also Φ_{Ph}) rises. For 4BrPS matrix the variation turns out to be stronger. Analogous results were obtained also for TTA in matrices of PS, PC and 4BrPS. All results, concerning the effect of matrix density upgrowth, due to both polymer change and pressure application, on luminescence properties of TTA and TPD, point out to the increase in probability of just the S_1–T_1 intersystem crossing, whereas the rates of both emissive and radiationless T_1–S_0 transitions remain almost invariable. This increase in probability of S_1–T_1 transition may likely be caused by (a) reinforcement of the effects induced by mixing of wave functions of amine molecule and polymer segments under diminution of intermolecular distances, that is particularly expressed, when 4BrPS was used instead of PS (Fig. 7); (b) change in spatial structure of amine molecule, that is evidenced by vibronic structure smoothing in luminescence spectra of doped polymers in comparison with spectra of proper toluene solutions (Figs. 4–6).

CONCLUSION

Thereby, by means of luminescence analysis of toluene solutions and doped polymer films it was shown that lowering of energy separation between S_1 and T_1 molecular levels within the wide set of phenyl-substituted amines results in fall of fluorescence yield, that is accompanied by phosphorescence yield rise and decrease in its decay time. This behaviour is mainly caused by strengthening of intersystem crossing, which may become a predominant process of energy relaxation of S_1 state. Other factor influencing on its efficiency is a structural one conditioned by non-planar and unrigid molecular conformation of amines. The probabilities of intersystem S_1–T_1 and T_1–S_0 transitions are also essentially depend on interaction with ambient medium, that gains especial strength when polymer matrix contains a heavy atom of bromine. In addition, the rate of S_1–T_1 intersystem crossing in TTA and TPD molecules increases upon rise of density of solid matrix, when the polymer matrix is changed or pressure up to 3 kbar is applied. This effect is connected with more effective mixing of molecular wave functions of amine and polymer segments due to decrease in intermolecular distances and/or distortion of molecular structure of amine.

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