THE JOURNAL OF CHEMICAL PHYSICS **130**, 074501 (2009)

The photophysics of singlet, triplet, and degradation trap states in 4,4-*N*,*N*′-dicarbazolyl-1,1′-biphenyl

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(Received 10 June 2008; accepted 5 January 2009; published online 17 February 2009)

In this paper we report the results of optical characterization of 4,4-*N*,*N*′-dicarbazolyl-1,1′-biphenyl (CBP), known as a host material for phosphorescent light emitting devices. Using absorption, steady state, and time-resolved spectroscopy, we explore the singlet and triplet states in solid and solution samples of CBP. In solutions we observe two distinct short-lived states with well-resolved emission originating from individual molecule singlet states (at 365 and 380 nm) and "quenching" low energy (LE) states (at 404 and 424 nm). The latter are seen only in saturated solutions and solid samples. Both of those species have different lifetimes. After UV exposure of very concentrated degassed solution the intensities of the LE bands starts to decrease. The longer the solution is exposed to UV, the less emission is seen at 404 and 424 nm, until it is totally gone. The spectrum of the highly concentrated solution is then the same as the spectrum of dilute solution, i.e., only emission at 365 and 380 nm is present. An increase in intensities of the singlet emission peaks correlates with an increase in UV exposure time. Similar behavior is observed in evaporated CBP film. We propose that this behavior is due to chemical instability of the weak N–C bonding of carbazolyl moiety—this creates new degradational species over time which dissociate after exposure to UV. We believe this to be the reason for variation in CBP fluorescence and delayed fluorescence spectra recorded by various research groups. Further, we detected two types of very long-lived states. One of these states (higher energy) is ascribed to molecular phosphorescence emission, the other to emission from low energy triplet trap states which we relate to degradational species. We propose that triplets are more easily caught by these latter sites when their hopping rate increases, and they emit inefficiently from these lower energy sites. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3077163]

I. INTRODUCTION

Recently there has been much effort put in to enhancing phosphorescent organic light emitting devices (PHOLED).[1–3] The light in this type of OLED comes not only from singlet excitons which amount to 25% of all excitons created but also from 75% triplet excitons also created.[2] In conventional OLEDs vanishingly small radiative decay rates of triplets impose a fundamental 25% limit to internal quantum efficiency. This is overcome in PHOLEDs as the host material is doped with heavy transition metal-ligand complexes, in which spin-orbit coupling mixes singlet and triplet states to yield highly phosphorescent molecules.[2] In order to improve the efficiencies of PHOLEDs it is important to understand how triplets behave in organic materials and the quenching mechanisms, especially arising from the host, which is used in PHOLED manufacture. There are other triplet loss mechanisms in the PHOLEDS, one of them being triplet loss via triplet-triplet annihilation (TTA).[4] The TTA process is particularly useful as the singlet manifold is repopulated via triplet annihilation, yielding delayed fluorescence whose decay dynamics can be easily measured and as well diffusion coefficients can be extracted from that information.[4] So it is essential to understand quenching mechanisms and delayed fluorescence in host materials in order to evaluate whether the material is suitable for using as host in PHOLEDs or when calculating diffusion coefficients of triplet migration.

One of the most popular host materials used for red, yellow, green, as well as blue emitters in PHOLEDs is 4,4-*N*,*N*′-dicarbazole-1,1′-biphenyl (CBP).[2,5–7] Triplet loss due to triplet annihilation is an issue in CBP and efforts have been made to explore TTA decay rates in CBP by observing delayed fluorescence, in thin films, centered at 410 and 430 nm.[4] CBP triplet migration diffusion coefficients have been calculated for CBP using the information conveyed via delayed fluorescence decay.[4] However, in solution the CBP fluorescence spectrum has peaks at 365 and 380 nm, and one could not expect the singlet emission to shift to the red by such a large amount of energy just because of going from liquid to solid state. In addition, one can also find discrepancies among various research groups' measurements of optical properties of CBP film, especially for fluorescence and delayed fluorescence spectra.[4,8–14] In this work we explore and discuss very unusual absorption, fluorescence, phosphorescence, and delayed fluorescence properties of vacuum sublimed commercially available CBP, how it is affected by aging and UV light, and propose the origin of the redshifted peaks at 410 and 430 nm.

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II. EXPERIMENTAL

All samples were thermally evaporated using a commercial Kurt Lesker Spectros II deposition system consisting of a vacuum (down to 1×10^{-8} mbar) chamber, six low temperature organic evaporation sources, three metal evaporation sources, quartz sensors to measure the deposition rate, and thickness of evaporation, substrate holder, which is normally rotated during the evaporation. All processes are controlled via special software enabling complex OLED device fabrication by sequentially depositing up to six different organic layers as well as metallic cathode without breaking the vacuum. There is also a possibility to coevaporate layers, i.e., to dope a host by evaporating two materials at the same time. Vacuum sublimed CBP was received from our industrial partner and used without further processing. Thin films were evaporated on quartz substrates of 12 mm diameter. Solutions of CBP were made in toluene. Steady state absorption spectra and luminescence emission and excitation spectra of solutions and thin films were recorded using a UV/vis spectrophotometer (Lambda 19 from Perkin Elmer) and commercial spectrofluorimeter (Fluorolog from Jobin Yvon), respectively. Gated luminescence and lifetime measurements were made using a system consisting of excitation source, pulsed yttrium aluminum garnet (YAG) laser emitting at 355 nm (EKSMA or CryLas GmbH).[15] Samples were excited at 45° angle to the substrate plane and the energy of each pulse could be tuned from microjoules up to millijoules, the diameter of the beam falling on the sample was about 0.6 cm. With the help of a spectrograph and other optics luminescence was collected onto a sensitive intensified charged-coupled device camera (Stanford Computer Optics) with subnanosecond resolution.[15] For low temperature measurements (down to 12 K) samples were placed in a cryostat.

III. RESULTS

A. Absorption properties

First, the absorption dependence on concentration of CBP in toluene (chemical structure of CBP can be found in Supporting Information[16]) was measured. In Fig. 1(a) the spectra of solutions with different concentrations are shown. The sharper peak at 295 nm could be attributed to carbazole moiety[17] and the broad region centered on 320 nm may be attributed to the π-π^* transition. The region between 382 and 413 nm of higher concentrated solutions is depicted in Fig. 1(b) and a peak around 393 nm for highly concentrated solutions is seen, whereas for lower concentrations it is absent. Absorbance dependence on concentration at 340 and at 393 nm is linear. The absorption coefficient at 340 nm is approximately 23 000 $M^{-1}\,cm^{-1}$, whereas at 393 nm ~16 $M^{-1}\,cm^{-1}$ that is about 1000 times smaller.

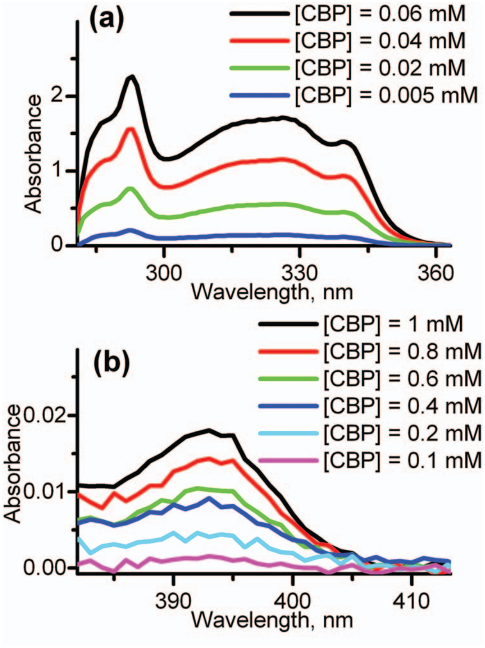

FIG. 1. (Color) Absorption spectra of CBP in toluene of (a) low concentrated solutions in region between 280 and 360 nm and of (b) highly concentrated solutions in region between 382 and 413 nm.

B. Excitation and emission properties

The excitation spectra of CBP solutions confirm our findings of 393 nm peak in absorption studies. The excitation spectrum (emission collected at 381 nm) of low concentration CBP solution (1.7 μM) has a broad band at about 320–330 nm (Fig. 2). As the concentration of CBP in solution is increased a new peak at 360 nm grows in. This is an artifact (due to inner filter effect) of the experimental setup as a result of the way light is collected (90° between excitation and emission paths). But when the concentration is increased even more and the emission is collected at 468 nm, a new peak near 393 nm in the excitation profile is seen which is in agreement with the absorption spectrum.

Emission studies as well show concentration dependent luminescence properties. At very low concentrations (0.002 mM) and exciting at 320 nm, the CBP solution luminescence exhibits two peaks: at 365 and 380 nm (Fig. 3). Since the concentration is very low this has to be the emission from individual CBP molecules, and we ascribe these peaks to CBP individual molecule singlet emission (singlet emission bands). When the concentration is increased up to 0.85 mM the emission band broadens. We observe two small bands growing around 404 and 424 nm and two new well-resolved peaks out of those bands at 404 and 424 nm when the concentration is increased up to 1.7 mM. We term those bands

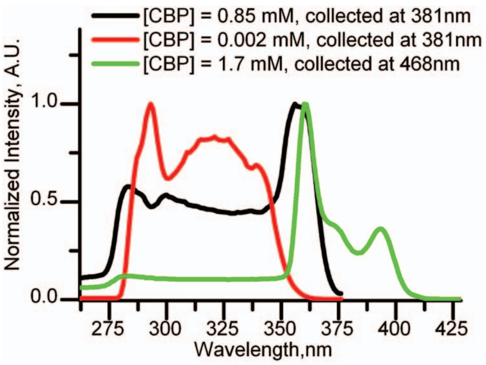

FIG. 2. (Color) Normalized excitation spectra of CBP in toluene at various concentrations.

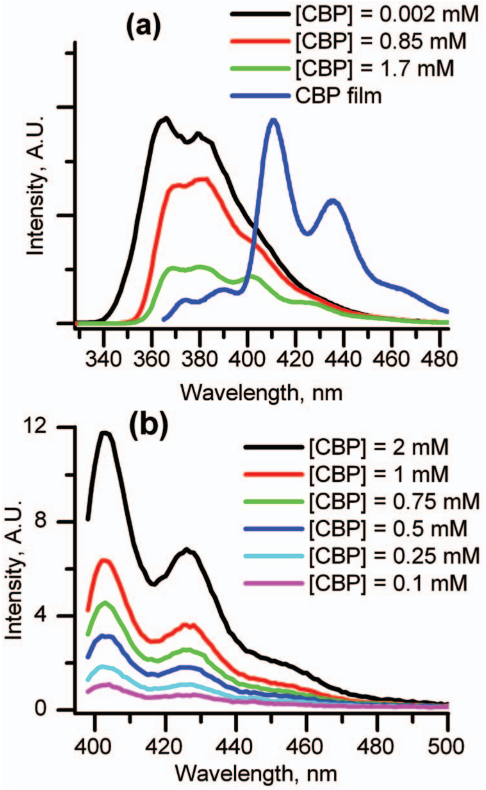

FIG. 3. (Color) Steady state emission spectra of CBP in toluene at various concentrations at two excitation wavelengths of (a) 320 and (b) 393 nm. For comparison purposes CBP film photoluminescence spectrum in (a) is added (the intensity is offset for clarity).

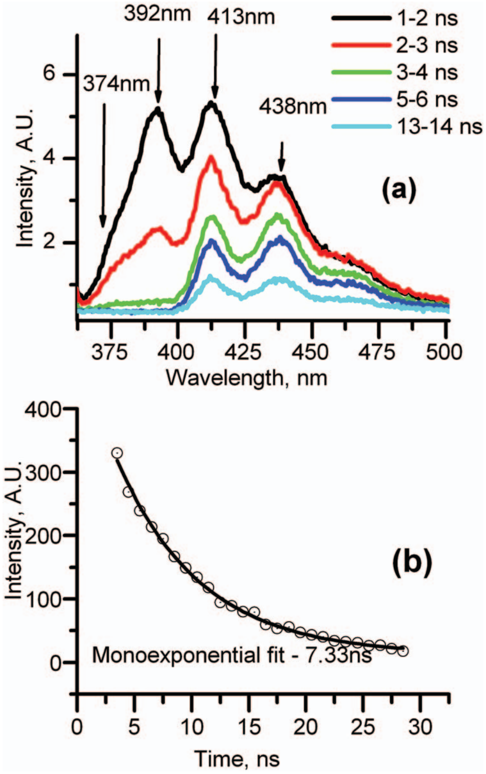

FIG. 4. (Color) (a) Time-resolved spectra of CBP film, thickness of 250 nm, evaporation rate of 0.5 A/s, measured at 12 K, excitation with YAG third harmonics, camera opening, and closing time after excitation are indicated. (b) Photoluminescence decay (open circles) of CBP film, intensity integrated from 405 to 460 nm. Black solid line corresponds to monoexponential fit.

lower energy (LE) bands. The overall intensity decrease with an increase in concentration may be the artifact of the measurement because of very high concentrations.[18] However, relative decrease in the peak at 365 nm in comparison to 380 nm cannot be due to such an artifact, and it may indicate that CBP singlet emission is quenched in the higher concentrated solution by the state which absorbs at 393 nm and is re-emitted via LE bands [recall Fig. 1(b) and compare in Fig. 3(a) or in normalized emission spectra in Supporting Information[16] Fig. S2].

The luminescence spectrum of thin film has as well four peaks, however, they are all redshifted by approximately 10 nm, which is reasonable [Fig. 3(a)]. Two higher energy peaks at 374 and 392 nm in analogy to CBP in solution can be ascribed to CBP individual molecule singlet emission (singlet emission bands) and two LE peaks at 413 and 438 nm can be ascribed to LE bands. Most important is that the relative intensities of LE bands (compared to singlet emission bands) in film are higher than the relative intensities of LE bands (compared to singlet emission bands) in solutions. This as well indicates that the species giving rise to the LE bands act as a quenchers of singlet excitons. Thus the more concentrated the solution, the higher the LE band relative intensity, being highest in a thin film. It is important to note that the lifetime of LE bands in solid state is much longer ~7 ns (Fig. 4) than the lifetime of peaks at 374 and 392 nm which according to the literature should be smaller than 1 ns (Ref. 19), thus showing a different origin for these states. For the moment we draw the reader's attention to these LE states centered in thin film as the "delayed emission" from these states has been interpreted as a sign of TTA and has been used to probe TTA and calculate diffusion coefficients in other CBP studies.[4] However, as we have shown here, the species giving rise to these emission bands are different to the isolated CBP molecular species, and thus the LE emission is not delayed fluorescence arising from TTA from CBP triplet state.

To understand what gives rise to the LE features further measurements were made. The LE bands (404 and 424 nm in solution or 413 and 438 nm in solid state) at first sight do not look like excimer emission because normally in this case bands are structureless and much broader,[20] whereas here, we see two well-resolved features. It would be reasonable to think that these two peaks are due to dimer formation, and the new peak arising in the absorption spectra at high concentrations further supports this. However, as already mentioned above, the absorbance at 393 nm has a linear dependence on concentration which excludes the dimer model. We further tested this using fluorescence [exciting at the newly emerging absorption band at 393 nm, recall Fig. 1(b)], and the result is the same—LE band luminescence intensity increases linearly with the increase in concentration [Fig. 3(b) and Fig. S3 in Supporting Information[16]]. Thus we rule out excimer and dimer as the species responsible for the LE features.

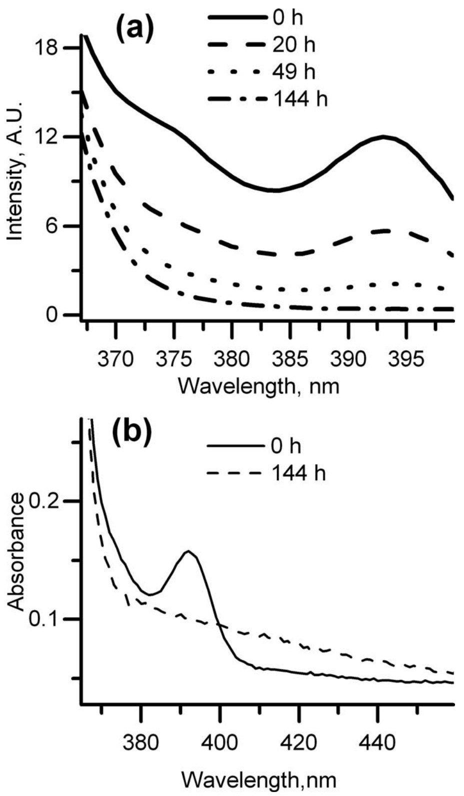

FIG. 5. UV light effect on (a) excitation spectra (light collected at 404 nm) and (b) absorption spectra of 1 mM CBP in degassed solution of toluene. Parameter is time in hours after exposure to UV light.

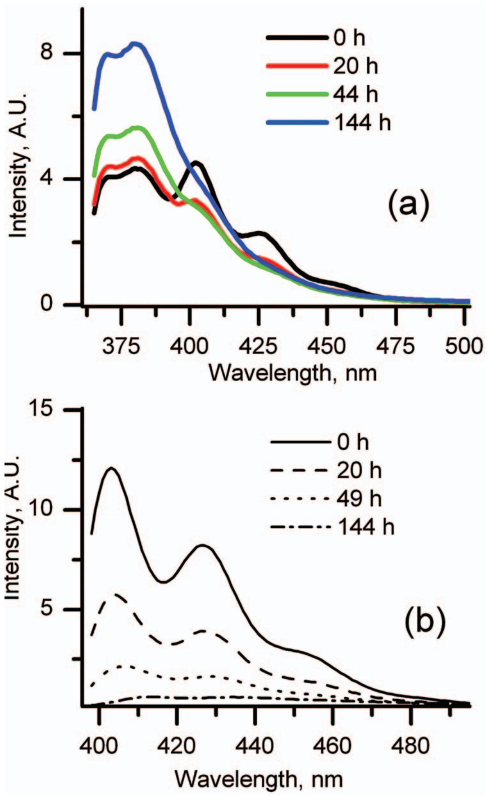

FIG. 6. (Color) UV light effect on emission spectra of 1 mM CBP in degassed solution of toluene when excitation wavelengths are (a) 355 nm and (b) 393 nm. Parameter is time in hours after exposure to UV light.

C. Effects of annealing and UV light on steady state spectra of CBP in solutions and films

One possible origin of LE states could be from degradation products of CBP, thus we made some effort to explore this. In a thorough study of CBP degradational mechanisms in devices and in thin films, Kondakov *et al.*[21] found that UV light can affect CBP. However, in this study there is no any account of how the photophysical properties of this materials change when exposed to UV light. So we studied how steady state absorption, excitation, and emission spectra of CBP in highly concentrated solutions and thin films are affected by UV light, hoping to get some insight on the origin of LE bands. Degassed, highly concentrated samples of ~1 mM were put under a UV lamp (8 W mercury lamp peaking at 365 nm). We recorded absorption, steady state excitation, and emission spectra after various periods of time under the UV lamp.

In the excitation and absorption spectra the peak at 393 nm diminishes with the increase in time under UV excitation (Fig. 5). The same tendency is seen in emission spectra where the LE bands gradually decrease and the singlet emission bands increase at the same time (Fig. 6). This again indicates that the LE states act as quenchers of the singlet emission bands as the absorption band at 393 nm overlaps strongly with singlet emission bands. It is interesting to note that when exciting at 393 nm, the LE band emission decreases exponentially with UV exposure time (Fig. S4 in Supporting Information[16]). The same tendency is seen when exposing thin films to UV light (Fig. 7). We observe the relative decrease in intensity of the LE states with the increase in UV exposure time. In this case one cannot completely extinguish these peaks with the UV irradiation probably due to lower UV penetration into film than into solution. For interpretation of this behavior and how it relates to the origins of LE bands, we refer to the discussion.

The effects of annealing on steady state spectra were also investigated, as this knowledge of photophysical changes in CBP may be quite important given that devices are annealed before operation. We recorded spectra of 100 nm thick CBP film capped with a 200 nm Al film before and after annealing in nitrogen for 5 h. The intensity of the spec-

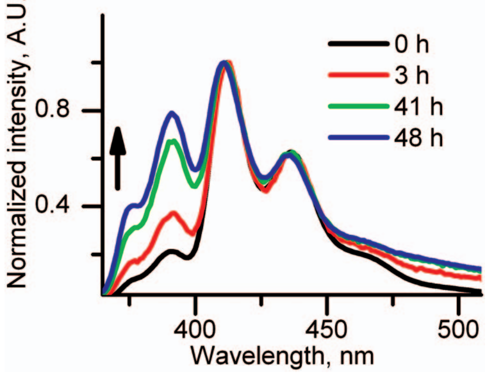

FIG. 7. (Color) Change in emission spectra of CBP thin film after exposure to UV light, excited at 355 nm. The arrow indicates the relative increase in peaks at 374 and 392 nm. Parameter is time in hours after exposure to UV light.

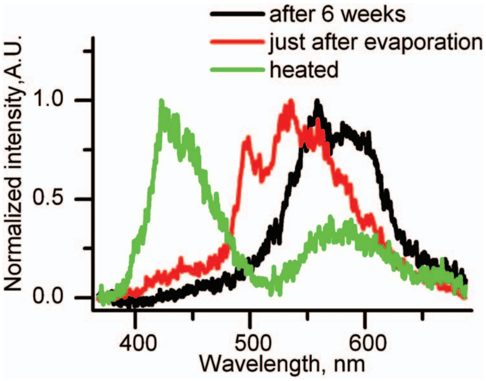

FIG. 8. (Color) Gated late emission spectra of evaporated CBP thin film, at 16 K, film just after evaporation (we ascribe it to phosphorescence), the same film 6–7 weeks after evaporation and later heated at 381 K for 3 h. All spectra recorded 20 ms after excitation.

trum roughly stays the same; however, the singlet emission peak at ~374 nm deceases in relation to the LE bands and the latter shifts to the red by ~4 nm (Fig S5 in Supporting Information[16]). We would like to stress that normally luminescence spectra tend to redshift for more ordered materials, such as would arise after annealing processes.

D. Triplet state of CBP

If it is to be successfully used as a host for phosphorescent dopants, it is very important to fully investigate the triplet state properties of CBP. The triplet level (at the onset) of CBP in frozen toluene solution is located at 440 nm or 2.81 eV. Since the concentration of measured solution was very low, in the range of 1 μM, the phosphorescence spectra recorded are of isolated molecules interacting only with the solvent (toluene) (for spectra see Supporting Information[16] Fig. S6).

Measurements of triplet level of evaporated CBP were made (Fig. 8 red curve and Supporting Information,[16] Fig. S7). The phosphorescence spectrum of CBP film has four features at 497, 532, 560, and 607 nm. All these spectral components have the same lifetime, however, as will be shown later the states at 560 and 607 nm may have different origin to the real phosphorescence of the material. The triplet level (at the onset) of evaporated CBP on a quartz substrate is located at 475 nm (2.61 eV) which is redshifted in comparison to frozen solution phosphorescence measurements. The same CBP film sample was stored in an inert atmosphere and exposure to air was minimized. Then gated late emission spectrum of the same sample (Fig. 8 black curve) was recorded ~6 weeks after evaporation. The peaks at 497 and 532 nm are gone and all that is left are the features at 560 and 607 nm, both of which have the same lifetime.

Then the aged samples were heated for 3 h at 381 K in a low vacuum of approximately 10^{-2} mbar. The normalized gated late emission spectrum of the heated sample is plotted in Fig. 8 as a green curve. The intensity of features at 560 and 607 nm after heating decreased, but now one can observe a new band at around 420 nm, while before heating it is clearly not present. Since it is observed 20 ms after excitation we ascribe this to delayed fluorescence[4] and this must imply higher triplet mobility after heating of the film. We assume that this delayed fluorescence is more likely to come from the LE states (at 413 and 438 nm in film) rather than singlet emission states (at 374 and 392 nm in film). Higher triplet mobility would also imply that more triplet excitons are caught in trap states in heated film than in unheated and unaged film. We suspect trap states to be around the energies of 2.2 eV (560 nm) and 2.0 eV (607 nm). This is further supported by the observed temperature dependence of CBP triplet spectra (Fig. 9).

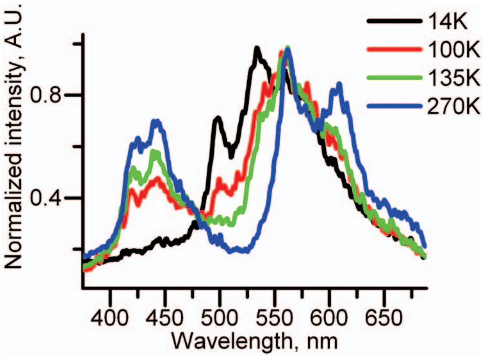

FIG. 9. (Color) Temperature dependence of late emission spectra of evaporated CBP thin film, thickness of 250 nm. All spectra recorded 20 ms after excitation.

At the higher temperatures (110–270 K) we have higher mobility of triplets thus more delayed fluorescence and more trap state emission at 2.2 eV (560 nm) and 2.0 eV (607 nm), while at low temperature, 14 K, we observe virtually no delayed fluorescence, i.e., low triplet mobility, and only see phosphorescence emission from the states 2.49 eV (497 nm) and 2.33 eV (532 nm). Similar spectra, measured at 125 K, have been presented by others as well, having a peak at 560 nm (which was ascribed to phosphorescence) as well as peak at 420 nm ascribed to delayed fluorescence from TTA.[11]

IV. DISCUSSION

The question as to why people observe such a variety of steady state spectra of solid CBP is very intriguing. Some solid state spectra are reported with vibronic peaks at around 375 and 390 nm (Refs. 9, 12, and 13) or only at around 390–400 nm,[8,10] while others report spectra with an additional peak at around 410 nm (Refs. 11 and 14) and some ascribe the bands at 410 and 430 nm (or 420 nm) to delayed fluorescence of CBP film.[4,11] We ruled out the formation of dimer or excimer species being responsible for the LE features, thus the other assumption is that some degradation products are responsible for them. Indeed, this may be true, since Kondakov *et al.*[21] proposed degradation mechanism specifically for CBP and suggested that degradation is due to breaking of the N–C bond between aryl and carbazolyl radicals. Density functional calculations, performed by them, showed that the dissociation of this bond should take place with an excitation energy of approximately 3.65 eV,[21] which is close to singlet emission energy of ~3.4 eV (in solution). Taking into account other evidence[21] presented by this group, it is very likely that CBP degradation (which also occurs in OLEDs) takes place via the dissociation of this bond in the

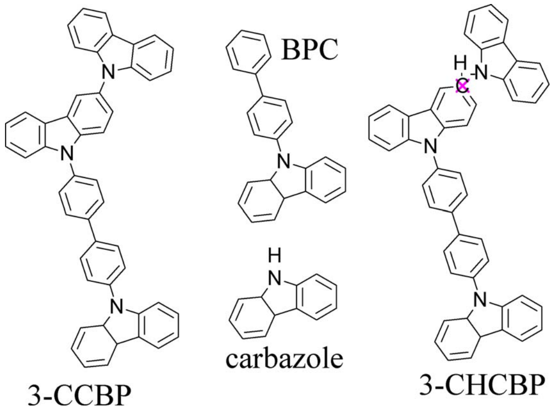

FIG. 10. (Color online) Chemical structures of possible degradational products (3-CCBP (3-carbazole-4,4′–bis(*N*-carbazolyl)biphenyl), carbazole and BPC (carbazolyl, 4-(*N*-carbazolyl)biphenyl)) as well as one proposed intermediate product 3-CHCBP, adopted from Ref. 20.

excited state. Kondakov's[20] high pressure liquid chromatography/mass spectrometry (HPLC/MS) as well as ^{1}H NMR analysis of CBP in devices after device operation and of CBP films after their exposure to UV showed that one can detect an array of different molecules other than CBP present in the samples (Fig. 10).[21] For example, they found that it could be carbazolyl, BCP or 3-carbazole-4,4′–bis(*N*-carbazolyl)biphenyl (3-CCBP).[21] As it can be easily identified from molecular structures of detected chemical products, those molecules can be formed if one has breakage of N–C bond between aryl and carbazole radicals of CBP. It is very important to note that even the pristine samples could have these type of products if they where exposed to UV photons. As well, because of the innate nature of degradation mechanism they can easily appear during the measurement process when intense UV light is used for excitation. That is why such a variety of CBP film fluorescence and delayed fluorescence spectra have been recorded by others.[4,8–14] So it is reasonable to assume that the quenching LE states we have observed may have resulted from CBP dissociation due to this weak C–N bond over time. However, the species formed due to such degradation are themselves unstable because of the same C–N bond, and after illumination with UV for a long enough time they photodegrade into nonemissive species, reducing the LE band emission.

The other question is, where do the CBP triplet trap states at 560 and 607 nm come from? The most likely, that those trap states are triplet states from the same degradation species which are responsible for LE band emission i.e., it is triplet emission of degradational product. LE band peak energies in solid film are 3 eV (~413 nm) and 2.83 eV (~438 nm), and the difference between them is equal to 0.17 eV [see e.g., Fig. 3(a) blue curve]. From Fig. 9, 270 K curve, the difference between peaks of trap state energies of 2.21 eV (560 nm) and 2.04 eV (~607 nm) is as well 0.17 eV. Normally triplet emission bands are an image of singlets, which is the case this time. As a consequence we relate triplet trap states with the species producing the LE bands. In Fig. 11 we give a Jablonski diagram depicting the state levels for a thin film. From the same Fig. 3(a) or Fig S2 in Supporting Information,[16] it is clear to see that the vibronic spacing of CBP molecular singlet species in film is 0.16 eV, i.e., a carbon double bond stretch mode. The peak energies of 2.49 eV (497 nm) and 2.33 eV (532 nm) of CBP molecule triplets (the phosphorescence) are also 0.16 eV (Fig. 8 red curve). Now the behavior of late delayed emission in film at various temperatures becomes more clear (recall Fig. 9). At the higher temperatures (110–270 K) we have higher mobility of triplets and more migration to the low concentrated triplet trap states, and as a consequence more delayed fluorescence and more triplet trap state emission at 2.2 eV (560 nm) and 2.0 eV (607 nm) is observed. While at low temperature, 14 K, we observe virtually no delayed fluorescence emission from LE species, i.e., low triplet mobility so little population of triplet trap sites, and we only see CBP phosphorescence emission from the states at 2.49 eV (497 nm) and 2.33 eV (532 nm). We would like to stress that no delayed fluorescence related to molecular CBP species (around 374 and 392 nm) has been observed. This fits well with the late emission spectra results of heated or aged CBP. We suspect that the increase in triplet mobility is due to the change in conformation of the CBP crystallites (more ordered) during comparatively long storage time or while the sample is heated during very short time. Indeed one expects a more ordered structure since the molecules have enough energy to reorient themselves into more favorable—ordered—positions. The observed behavior of triplet states could be confirmed by theoretical considerations in a nice paper by Richert and Bassler[22] which are as follows. In a more ordered structure, the Gaussian distribution width of the density of energy states is narrower. According to dispersive triplet migration theory,[22,23] the smaller the Gaussian width of distribution, the higher the dispersion parameter, and the higher the dispersion parameter, the higher the hopping rate of triplet excitons becomes in a film. This results in an increased probability to reach a trap state even if the trap density is comparatively low as migrating excitons can easily find them. A more ordered structure also results in an increased annihilation rate, yielding those singlets responsible for delayed LE band fluorescence. The redshift of steady state emission in the CBP films after heating may too confirm that CBP becomes more ordered after exposure to higher temperatures.

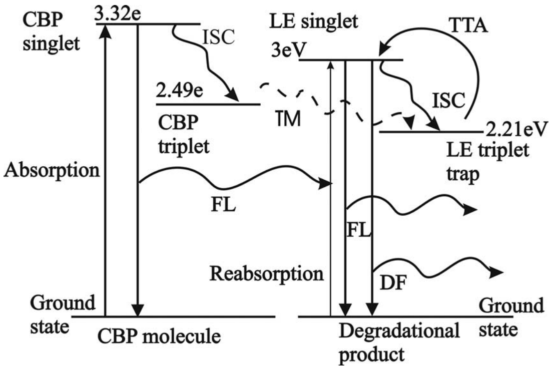

FIG. 11. Proposed Jablonski diagram for CBP thin film. ISC stands for intersystem crossing, TM: triplet migration; TTA: triplet annihilation; LE: low energy bands. Levels are determined taking the peak energy of first vibronics (not the onsets).

The consequences of even small amount of traps in the material can have crucial effect on the photophysical properties and OLED device performance. The increase in the emission intensity from trap sites looks similar to the effects of keto defects in polyfluorene,[24] where one sees large increases in a LE, broad peak in solid state in comparison to solution and where longer wavelength peaks act as luminescence quencher sites via energy transfer mechanisms.[25] The quenching is so effective that very large changes in emission color of the material may be observed as in CBP. Castex[26] observed the photodegradation under UV light illumination of the carbazole derivative N,N-diethyl-3,3-bicarbazyl, causing the emergence of a new emission band between 400 and 500 nm. It was proposed that phototransformation may have occurred via formation of carbazolylium N-oxide species.[26] Those trap states may appear in the device after long enough operation or annealing, resulting in the decrease in electrophosphorescence efficiency seen by others.[21]

V. SUMMARY

CBP was characterized by steady state absorption, emission and excitation steady state, as well as time-resolved spectroscopies. Using steady state absorption spectroscopy we observed peaks at 295 nm (carbazole moiety) and 320 nm (π-π^* transition) of CBP in toluene. As the concentration of CBP in solution is increased we also observe an absorption peak at 393 nm. The same peak is present in the excitation spectrum of highly concentrated CBP solutions. Dilute CBP solution exhibits two peaks: at 365 nm and at 381 nm which we ascribe to (individual) molecule singlet emission, whereas when concentration is increased, two new bands at 404 and 424 nm emerge (LE peaks). In thin film of CBP all these bands redshift including the LE bands which shift to 413 and 438 nm, respectively. Our experimental results as well as the variety of CBP fluorescence and delayed fluorescence spectra recorded by other research groups show that conventionally used commercial CBP (even vacuum sublimed "pristine" sample) is not very stable and probably dissociates into carbazolyl-type moieties over time. Under UV light, these degradation products themselves can be degraded and the corresponding peaks decrease considerably. We determined that the true triplet level (at the onset) of CBP in frozen solution is 2.81 eV (440 nm) and it redshifts (at the onset) in an evaporated CBP film to 2.61 eV (475 nm). Our measurements show that annealing and aging affect phosphorescence emission by increasing the fraction emitting from trap states and/or delayed fluorescence. The delayed emission observed in CBP films by others and ascribed to delayed fluorescence is showed here to be not from the pure CBP film singlet emissive states but probably from the degradation product species. Chemical analysis performed by Kondakov *et al.*[21] proved that CBP indeed is not very stable. HPLC/MS as well as ^{1}H NMR analysis of CBP in devices after device operation and of CBP films after their exposure to UV showed that one can detect an array of different molecules in the samples other than CBP such as BCP or 3-CCBP.[21] As it can be easily identified from molecular structures of detected chemical products, those molecules can be formed if one has breakage of N–C bond between aryl and carbazole radicals of CBP. Thus we relate LE species as well as triplet trap states to these degradational products. These states, even if the concentration is very low, may act as trap states to fluorescent dopants and decrease the efficiency of CBP via exciton migration in film, especially of triplet states. The relatively long-lived emission intensity from these low energy triplet traps increases after annealing or aging. Consequently, the lifetime of devices with CBP as a host for phosphorescent emitters may be decreased and have low efficiency due to triplet exciton quenching.

ACKNOWLEDGMENTS

The authors thank the Eastman Kodak Co. for the materials and also Kodak European Research for the studentship for V.J.

[1] B. W. D'Andrade, J. Brooks, V. Adamovich, M. E. Thompson, and S. R. Forrest, Adv. Mater. (Weinheim, Ger.) **14**, 15 (2002).
[2] Y. Sun, N. C. Giebink, H. Kanno, B. Ma, M. E. Thompson, and S. R. Forrest, Nature (London) **440**, 908 (2006).
[3] B. W. D'Andrade, S. R. Forrest, and A. B. Chwang, Appl. Phys. Lett. **83**, 3858 (2003).
[4] N. C. Giebink, Y. Sun, and S. R. Forrest, Org. Electron. **7**, 375 (2006).
[5] B. J. Chen, X. W. Sun, and K. R. Sarma, Mater. Sci. Eng., B **139**, 192 (2007).
[6] M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, and S. R. Forrest, Appl. Phys. Lett. **75**, 4 (1999).
[7] V. Adamovich, J. Brooks, A. Tamayo, A. M. Alexander, P. I. Djurovich, B. W. D'Andrade, C. Adachi, S. R. Forrest, and M. E. Thompson, New J. Chem. **26**, 1171 (2002).
[8] F. Li, M. Zhang, G. Cheng, J. Feng, Y. Zhao, Y. Ma, S. Liu, and J. Shen, Appl. Phys. Lett. **84**, 148 (2004).
[9] J. Yu, H. Zhang, L. Zhou, R. Deng, Z. Peng, Z. Li, L. Fu, and Z. Guo, J. Lumin. **122–123**, 678 (2007).
[10] D. Schneider, T. Rabe, T. Riedl, T. Dobbertin, M. Kröger, E. Becker, H.-H. Johannes, and W. Kowalsky, Appl. Phys. Lett. **85**, 1886 (2004).
[11] C. Adachi, M. A. Baldo, and S. R. Forrest, J. Appl. Phys. **87**, 8049 (2000).
[12] T. Yu, W. Su, W. Li, R. Hua, B. Chu, and B. Li, Solid-State Electron. **51**, 894 (2007).
[13] T. Tsuboi, H. Murayama, S.-J. Yeh, and C.-T. Chen, Opt. Mater. **29**, 1299 (2007).
[14] G. Ramos-Ortiz, Y. Oki, B. Domercq, and B. Kippelen, Phys. Chem. Chem. Phys. **4**, 4109 (2002).
[15] C. Rothe and A. P. Monkman, Phys. Rev. B **68**, 075208 (2003).
[16] See EPAPS Document No. E-JCPSA6-130-009907 for supporting information. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
[17] Q. Zhang, J. Chen, Y. Cheng, L. Wang, D. Ma, X. Jing, and F. Wang, J. Mater. Chem. **14**, 895 (2004).
[18] J. R. Lakowitz, *Principles of Fluorescence Spectroscopy* (Kluwer Academic, New York/Plenum, New York, 1999).
[19] Y. Kawamura, H. Yamamoto, K. Goushi, H. Sasabe, and C. Adachi, Appl. Phys. Lett. **84**, 15 (2004).
[20] P. A. Losio, R. U. A. Khan, P. Gunter, B. K. Yap, J. S. Wilson, and D. D. C. Bradley, Appl. Phys. Lett. **89**, 041914 (2006).
[21] D. Y. Kondakov, W. C. Lenhart, and W. F. Nichols, J. Appl. Phys. **101**, 024512 (2007).
[22] R. Richert and H. Bassler, J. Chem. Phys. **84**, 3567 (1986).
[23] C. Rothe and A. P. Monkman, Phys. Rev. B **65**, 073201 (2002).
[24] S. I. Hintschich, C. Rothe, S. Sinha, A. P. Monkman, P. S. de Freitas, and U. Scherf, J. Chem. Phys. **119**, 12017 (2003).
[25] F. B. Dias, M. Knaapila, H. D. Burrows, and A. P. Monkman, Macromolecules **39**, 1598 (2006).
[26] M. C. Castex, C. Olivero, G. Pichler, D. Ades, and A. Siove, Synth. Met. **156**, 699 (2006).