

Effect of carbazole–oxadiazole excited-state complexes on the efficiency of dye-doped light-emitting diodes

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Interactions between hole-transporting carbazole groups and electron-transporting 1,3,4-oxadiazole groups were studied by photoluminescence and electroluminescence (EL) spectroscopy, in blends of poly(N-vinylcarbazole) with 2-*tert*-butylphenyl-5-biphenyl-1,3,4-oxadiazole (PVK:PBD) and in random copolymers with carbazole and oxadiazole groups attached as side chains. Different excited-state complexes form in the blends, which exhibit exciplexes, and in the copolymers, which manifest electroplexes, due to topological constraints on the position of carbazole and oxadiazole units in the polymer. Both types of complex red-shift the EL spectra of the matrices compared with pure PVK homopolymer, although the shift is significantly greater for the electroplex. The presence of these complexes has a profound effect on the external quantum efficiency of dye-doped organic light-emitting diodes employing the blends or copolymers as matrices, as it strongly affects the efficiency of Förster energy transfer from the matrix to the dye. Single-layer devices doped with either coumarin 47 (C47), coumarin 6 (C6), or nile red (NR) were compared. Among the three dye-doped PVK:PBD devices, C6 doping yields the highest efficiency, while NR doping produced the most efficient copolymer devices, consistent with the degree of overlap between the EL spectrum of the matrix material and the absorption spectrum of the dye. © 2002 American Institute of Physics. [DOI: 10.1063/1.1469692]

I. INTRODUCTION

Thin-film organic light-emitting diodes (LEDs), based either on small molecules^{1–3} or polymers,^{4–10} are of great current interest due to their potential application in large-screen emissive flat-panel color displays or as white backlights for liquid crystal displays. To achieve optimal efficiency and device lifetime, the injection and transport of holes and electrons must be balanced, such that similar densities of the two carriers are achieved. Two general approaches can be employed to balance carrier injection and transport, both incorporating hole- and electron-transporting materials into a LED. One approach is to fabricate a multilayer device with discrete hole-transporting and/or electron-transporting layers.^{1,11} While effective, this approach has only limited applicability to polymers, which are generally deposited by spin coating; deposition of subsequent layers will typically dissolve the layers deposited earlier. A second approach is to mix hole- and electron-transporting materials into a blend,^{5,12} or to copolymerize

hole- and electron-transporting groups together,^{13,14} and prepare simple single-layer devices where the active layer performs hole transport, electron transport, and light emission. But when the electron-donating groups of the hole-transporting material and the electron-withdrawing groups of the electron-transporting material are brought into intimate contact, excited-state complexes can form, which alter the spectrum of the emitted light.

Two different classes of excited-state complexes important for LEDs have been documented in the literature. The first class are *exciplexes*,^{15–23} where a molecule or subunit in an excited state complexes with a complementary molecule or subunit in its ground state, but no substantial charge separation occurs. The second class are *electroplexes*,^{24–26} formed between complementary molecules or subunits carrying a charge (a hole on an electron-donating site, an electron on an electron-withdrawing site). When the two components of the complex are chemically identical, the excited species are termed *excimers* (excited-state *dimers*, versus exciplexes) and *electromers*^{27,28} (versus electroplexes). For planar aromatic molecules, the donor and acceptor moieties constituting an electroplex are thought to be separated by a larger distance (0.4–0.7 nm) than are the constituents of an exciplex (0.3–0.4 nm),²⁶ so the ability to form each of these excited-state complexes can be influenced by material structure. Photoexcitation does not normally generate free charge carriers (only when dissociation of excited states is facile,

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e.g., in a good photoconductor²⁹), so the emission signature of electroplexes is visible in the electroluminescence (EL) spectrum but not typically in the photoluminescence (PL) spectrum.^{24–28} Conversely, exciplexes are readily generated through photoexcitation, so their emission is visible in both EL and PL spectra.

The presence of exciplexes and electroplexes leads to a redshift of the emission relative to the pure hole or electron transport material (which may or may not contain excimers), altering the color of the device emission. Indeed, the observed EL spectrum can comprise emission from several species, with the relative intensities changing with voltage, leading to a broad and voltage-dependent emission spectrum.²⁶ For color display applications, it is more desirable to have a narrow and voltage-independent emission spectrum, to achieve saturated red, green, and blue colors. Such narrow emission can be achieved by doping the material with a low concentration (1% or less) of a suitably chosen dye.^{5,12,14,30} Ideally, nonradiative energy transfer proceeds efficiently from the matrix material to the dye,³⁰ leading to emission characteristic of the dye alone. Moreover, dye doping is an attractive route to patterned full-color devices, as the dyes may be deposited by ink-jet printing^{31,32} or masking^{33,34} onto, and subsequent diffusion into, a previously deposited layer of matrix material (polymer). However, the presence of excited-state complexes in the matrix alters the energy levels present, and may well impact the efficiency with which energy can be transferred to the dye, although this has not been previously investigated.

Poly(*N*-vinylcarbazole) (PVK) and oxadiazole compounds such as 2-*tert*-butylphenyl-5-biphenyl-1,3,4-oxadiazole (PBD) have been widely used as hole- and electron-transporting materials in both heterostructured^{11,35} and single-layer^{5,12–14,30} LEDs. Previous studies of LEDs have revealed excited-state complexes containing either carbazole^{12,16,18,22,36} or oxadiazole groups.^{2,20,21,25,26} In this article, we demonstrate that different types of excited-state complexes can form between carbazole and oxadiazole groups in simple blends of PVK and PBD (polymer:small molecule blends, PVK:PBD, which exhibit exciplexes), and in statistical copolymers containing carbazole and oxadiazole pendant groups (in which we find electroplexes). We then explore the substantial effect that these complexes have on the efficiency of energy transfer to emissive dyes.

II. EXPERIMENT

Figure 1 shows the molecular structures of PVK, PBD, and the statistical copolymers CPVKPVO and CPVKBVO. The copolymers were prepared by free-radical copolymerization from *N*-vinylcarbazole (NVK) and one of two oxadiazole-containing monomers: 2-phenyl-5-{4-[(4-vinylphenyl)methoxy]phenyl}-1,3,4-oxadiazole (PVO), or 2-(4-*tert*-butylphenyl)-5-{4-[(4-vinylphenyl)methoxy]phenyl}-1,3,4-oxadiazole (BVO). The PVO and BVO monomer syntheses, and the syntheses and characterization of the copolymers and PVK, PPVO and PBVO homopolymers used here have all been described in detail previously.¹⁴ PBD

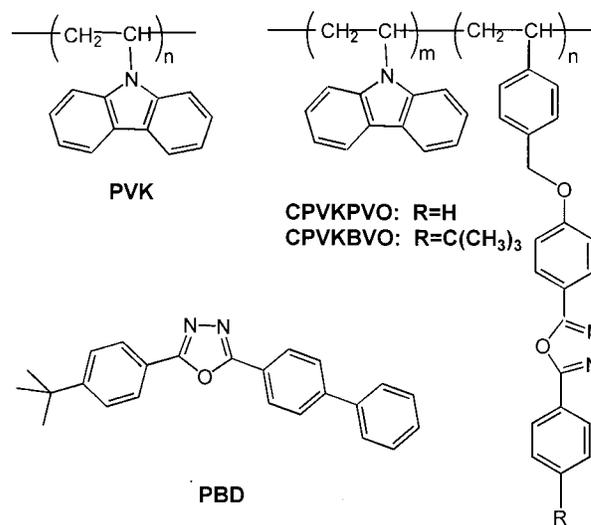


FIG. 1. Chemical structures of PVK, PBD, and the two types of copolymers employed in this work.

and nile red (NR) were purchased from Aldrich, coumarin 47 (C47) and coumarin 6 (C6) from Lambda Physik, and all were used as received.

Ultraviolet-visible (UV-vis) spectra of C47, C6, and NR were recorded for thin films on quartz substrates using a Hewlett-Packard 8452A diode array spectrophotometer. PL spectra of the blend and copolymer films on quartz substrates were taken with an Oriel InstaSpec IV charge coupled device (CCD) camera, using 316 nm excitation. Glass slides coated with indium–tin–oxide (ITO) (Applied Films Corp., 25 Ω/\square) were used as substrates for LED fabrication. The substrates were patterned and then cleaned by successive 5-min ultrasonications in detergent, de-ionized water, methanol, and chloroform, followed by treatment with oxygen plasma.³⁷ For LEDs with Mg:Ag as the cathode, a layer of the dye-doped or undoped PVK:PBD blends or copolymers was spin coated onto the substrate from a 28 mg/ml solution (total solids) in 1,2-dichloroethane (DCE) at 4000 rpm in a nitrogen glove box. The film thickness was 70–100 nm as measured by stylus profilometry. A 10:1 Mg:Ag cathode (100 nm) was deposited by thermal evaporation through a mask at 2×10^{-5} Torr. For LEDs with Ca as the cathode, the films were fabricated by spin coating a 15 mg/ml DCE solution at 2000 rpm, yielding films 55–80 nm thick. A 25-nm-thick Ca cathode was evaporated at 1×10^{-6} Torr. For devices with both Mg:Ag and Ca cathodes, a subsequent capping layer of 100 nm Ag was deposited at the same pressure. The active area of each device was about 8 mm². EL spectra of the LEDs were recorded using a Photo Research PR650 Photo-Scan Colorimeter (devices with Mg:Ag cathodes) or an Oriel InstaSpec IV CCD camera (devices with Ca cathodes). The device current and photon emission rate versus voltage characteristics were measured on a Hewlett-Packard 4155B Semiconductor Parameters Analyzer and a Newport 2835-C multifunction optical meter with a calibrated Si photodiode detector. Both EL and PL spectra are presented in radiometric units. Brightness in photometric units (cd/m²) was calculated from the forward output power and the EL spectra of

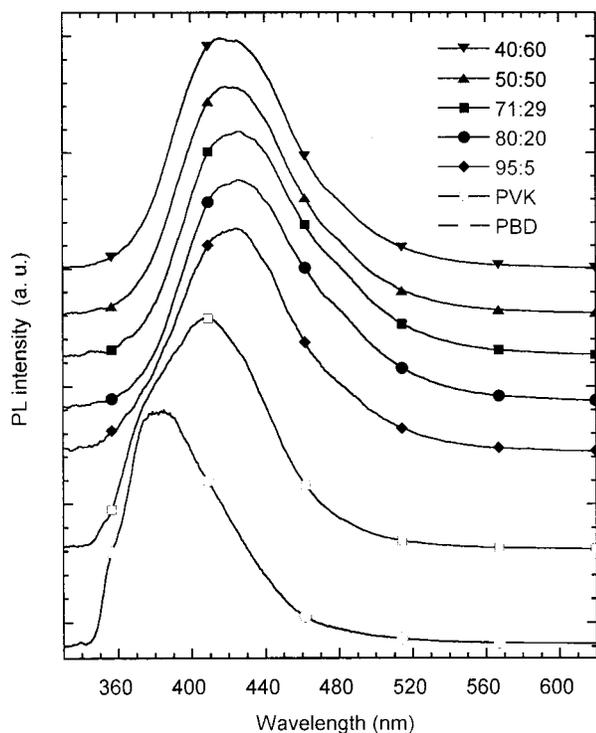


FIG. 2. PL spectra (excitation at 316 nm) of thin solid films of PVK, PBD, and PVK:PBD blends over a range of weight ratios. Curves are offset vertically for clarity.

the devices, assuming Lambertian distribution of the EL emission.³⁸

III. RESULTS AND DISCUSSION

A. Emission from undoped PVK:PBD blends

Figure 2 shows the PL spectra of thin solid films of PBD, PVK, and PVK:PBD blended at varying weight ratios. The PL maximum for PVK occurs at 410 nm, with a short-wavelength shoulder at 375 nm, due to emission from two different types of carbazole excimers.^{39,40} The PL maximum for PBD occurs at 380 nm, a slightly shorter wavelength than for PVK. By contrast, the PL spectra for all PVK:PBD blends, with weight ratios ranging from 95:5 to 40:60, show maxima at systematically longer wavelengths than either PBD or PVK: near 425 nm, essentially independent of composition, with an additional shoulder near 480 nm. While redshifts can reflect changes in the local polarization field induced by blending,⁴¹ this effect would produce a continuous spectral shift as the blend ratio is varied. Rather, the insensitivity to composition in Fig. 2 indicates that the redshift observed in the blend films results from exciplex formation.

Figure 3(a) shows the EL spectra of single-layer LEDs prepared with Mg:Ag cathodes from both PVK and PVK:PBD blend films. The EL maximum from the PVK device coincides with the peak in the PL from PVK (Fig. 2). By contrast, the EL from the PVK:PBD film is peaked around 440 nm, redshifted by about 30 nm compared with the EL or PL of pure PVK. These spectral differences are even more evident in Fig. 3(b), which shows EL spectra

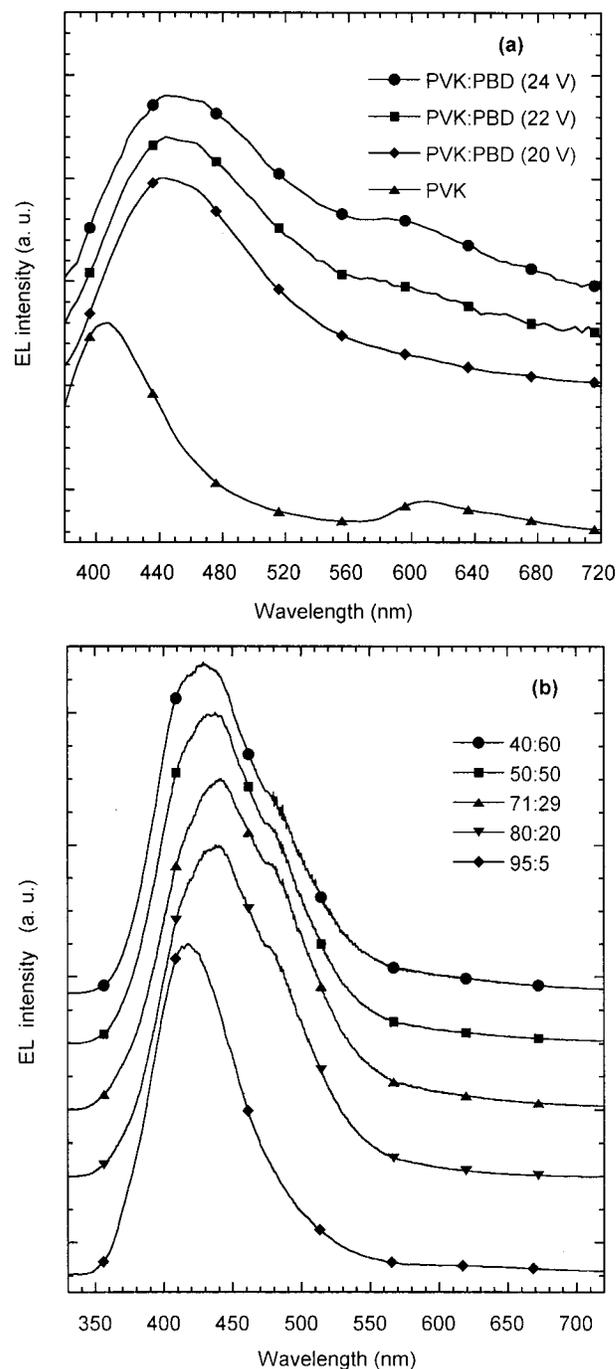


FIG. 3. (a) EL spectra of ITO/PVK/Mg:Ag and ITO/PVK:PBD(71:29)/Mg:Ag devices. EL spectra for the blend device are shown at three different drive voltages, as indicated. (b) EL spectra of ITO/PVK:PBD/Ca devices with varying blend weight ratios (PVK:PBD). The devices were forward biased at 12–14 V; corresponding current densities were 62–640 mA/cm², increasing monotonically with PVK:PBD ratio. Curves in (a) and (b) are offset vertically for clarity.

recorded with a more sensitive (CCD) detector, taken on blend devices (varying PVK:PBD ratios) fabricated with Ca cathodes and operated at 12–14 V forward bias. These higher-resolution spectra show a clear shoulder at 480 nm, which is also evident in the PL spectra in Fig. 2. Indeed, the PL (Fig. 2) and EL [Fig. 3(b)] spectra are quite similar, ex-

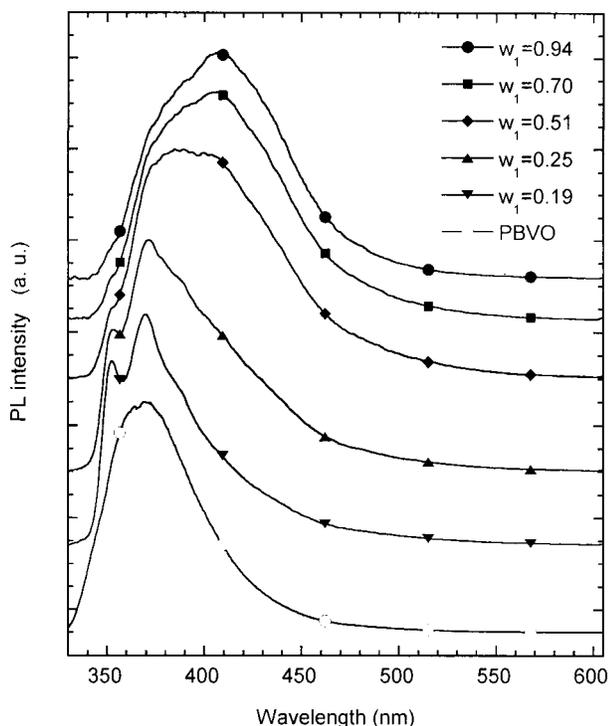


FIG. 4. PL spectra (excitation at 316 nm) of PBVO homopolymer and CPVKBVO copolymer thin films on quartz substrates. w_1 is the weight fraction of NVK in each copolymer. Curves are offset vertically for clarity.

cept for the blend most dilute in PBD (95:5), whose EL spectrum more closely resembles that of pure PVK [Fig. 3(a)]. The peak near 440 nm arises from PVK:PBD exciplexes,¹² and can be seen even in the emission from dye-doped PVK:PBD layers when energy transfer to the dye is incomplete.^{30,42}

The EL spectrum of PVK in Fig. 3(a) also exhibits a smaller peak at 610 nm, barely visible in the data acquired at lower voltages [Fig. 3(b)]. While this secondary emission has been seen in previous reports,^{5,16} its origin has not been elucidated. It is not due to triplet phosphorescence,^{40,43} which occurs near 500 nm. Here, we tentatively assign this emission to PVK electromers, as it is visible in the EL spectrum but not the PL spectrum. Additional support for this assignment is provided by the copolymer EL data, as discussed below.

B. Emission from undoped copolymers

Figure 4 shows the PL spectra of the PBVO and a series of CPVKBVO films on quartz substrates, where w_1 is the weight fraction of the NVK monomer in each copolymer. At high values of w_1 (0.70 and higher), the PL spectra for the copolymers are essentially those of PVK homopolymer (compare Fig. 2), with a maximum at 410 nm. The PBVO copolymer shows featureless emission peaked at 370 nm. By analogy with the blend PL spectra in Fig. 2, we would expect exciplex emission to appear in the PL spectrum of the copolymers at about 425 nm with a shoulder near 480 nm, but no such emission is evident in Fig. 4. Rather, as BVO units are added to the copolymer (w_1 reduced from unity), the spectra actually shift toward the blue. The PL spectra of the

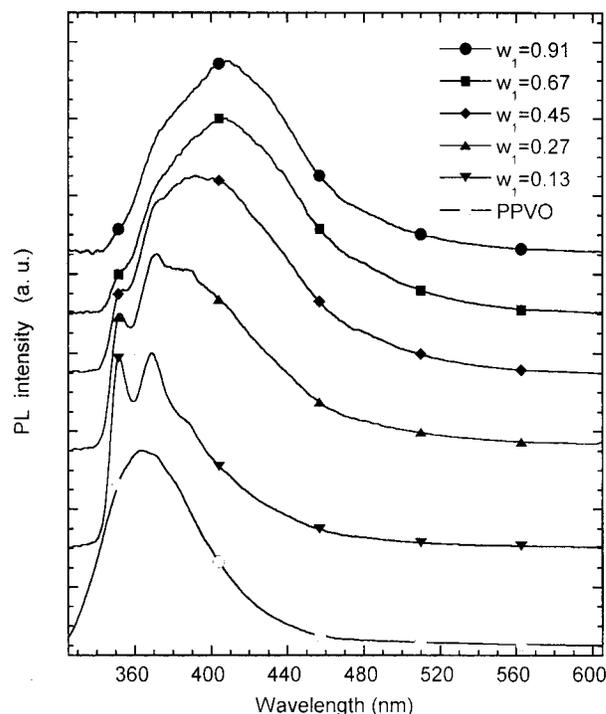


FIG. 5. PL spectra (excitation at 316 nm) of PPVO homopolymer and CPVKPVO copolymer thin films on quartz substrates. w_1 is the weight fraction of NVK in each copolymer. Curves are offset vertically for clarity.

copolymers at lower w_1 ($0.19 \leq w_1 \leq 0.51$) show a structured emission, with peaks or shoulders at 350, 370, and 390 nm. Indeed, the spectrum of the $w_1=0.19$ copolymer strongly resembles that for PVK model compounds (NVK dimers), where the peak at 350 nm is characteristic of isolated carbazole lumophores, and that at 370 nm from a weakly-bound excimer.³⁹ Emission from such structures is naturally more probable as the NVK content in the random copolymer is reduced.

The PL spectra from the other copolymer series (PVO homopolymer, CPVKPVO copolymers) are shown in Fig. 5, and exhibit the same trends evident in the CPVKBVO series, including a shift to the blue (rather than the red) as w_1 is reduced. We thus conclude that exciplex formation is inhibited in the copolymers relative to the blends, reflecting the topological constraints imposed by copolymerization and the need for complementary units to be spaced by 0.3–0.4 nm to form an exciplex. Fig. 1 shows that the carbazole units are connected directly to the polymer backbone, while the oxadiazole units are spaced out from the backbone by the phenylmethoxyphenyl group. Sequential NVK and BVO (PVO) units in the polymer chain will thus have little interaction; exciplex formation would only be possible between NVK and BVO (PVO) units from different chains, or from topologically distant sites on the same chain.

Figure 6(a) shows the EL spectra of ITO/CPVKPVO/Ca single-layer devices taken under a forward bias of 12–14 V. Compared with the PVK:PBD blends [Fig. 3(b)], the EL spectra of the pure CPVKBVO and CPVKPVO copolymers are very broad, spanning the whole visible range from 400 to 700 nm. The EL spectra of the copolymers each show three principal emission maxima: one at 370–440 nm, a second

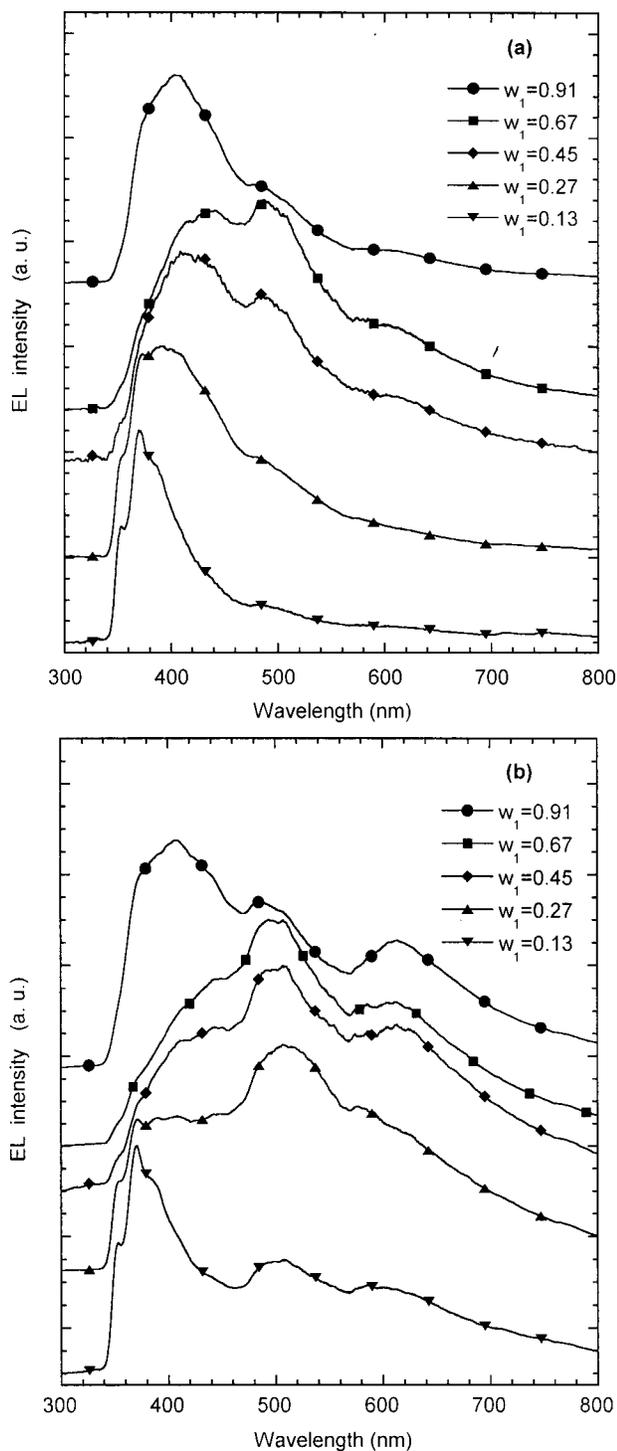


FIG. 6. (a) EL spectra of ITO/CPVKPVO/Ca devices under 12–14 V forward bias. w_1 is the weight fraction of NVK in each copolymer. Corresponding current densities were 1–50 mA/cm², increasing monotonically with w_1 . (b) EL spectra of ITO/CPVKPVO/Ca devices under 18–20 V forward bias. w_1 is the weight fraction of NVK in each copolymer. Corresponding current densities were 10–860 mA/cm², increasing monotonically with w_1 . Curves in both (a) and (b) are offset vertically for clarity.

near 500 nm, and a third near 610 nm. The shortest-wavelength maximum in each spectrum is the superposition of emission from isolated NVK and PVO segments and their excimers, and generally follows the trends seen in the copolymer PL spectra (Fig. 5). The smallest maximum, near

610 nm, is the same as that seen in the EL from PVK and PVK:PBD blend devices [Fig. 3(a)], attributed here to PVK electromers; note that the ratio of the intensity of this peak (relative to the band at 370–440 nm, which contains emission from both NVK and PVO units) increases steadily with w_1 , as expected for a PVK electromer. However, the peak near 500 nm has no analog in either the PVK homopolymer EL [Fig. 3(a)] or in the PL from the same copolymers (Fig. 5). We thus infer that this emission line results from NVK:PVO electroplexes. Because the donor and acceptor moieties constituting an electroplex are separated by a larger distance (0.4–0.7 nm) than are the members of an exciplex (0.3–0.4 nm), the topological constraints imposed by the polymer prohibit the formation of exciplexes between sequential units but not electroplexes.

For the copolymer devices, the emission was noticeably dependent on applied voltage: the emission was bluish green at lower voltages, but shifted continuously to yellow as the voltage increased. Figure 6(b) shows the EL spectra of the same ITO/CPVKPVO/Ca devices taken under a forward bias of 18–20 V, instead of the 12–14 V applied in Fig. 6(a). Increasing the drive voltage causes the electroplex (500 nm) to dominate the emission for most of the copolymers, while the PVK electromer emission near 610 nm increases in intensity as well. Careful examination of Figs. 6(a) and 6(b) shows that the relative intensity of the electroplex emission is greatest for the device made from the copolymer with $w_1=0.67$ for both drive voltages, and decreases smoothly as w_1 is varied in either direction from this optimum. Such behavior is consistent with emission from a heterocomplex, whose intensity must necessarily go through a maximum as the copolymer composition varies from pure NVK to pure PVO. Devices based on the CPVKBVO copolymers showed very similar EL spectra (representative example, $w_1=0.70$, shown in Fig. 7) to those for the CPVKPVO copolymers in Figs. 6(a) and 6(b), with the greatest relative intensity of the electroplex emission occurring at $w_1=0.51$ for both drive voltages.

C. Emission from dye-doped devices

Regardless of the nature of the excited-state heterocomplexes (exciplexes versus electroplexes), their presence in the blends or copolymers, directly revealed through the EL spectra, reflects populated energy levels that are not present in the pure components (PVK and PBD, or PVK and PBVO or PPVO homopolymers). Thus, we may consider the two types of complex together in assessing their effect on the efficiency of energy transfer to emitting dyes, the central focus of this article.

Compared with the best available organic LEDs, the EL emission from undoped PVK:PBD blends, or CPVKBVO or CPVKPVO copolymers, is weak for either cathode material, but the efficiency can be greatly improved by doping with an appropriate dye. Devices having either PVK:PBD blend⁵ or CPVKBVO copolymer¹⁴ matrices, doped with either coumarin 47 (C47, blue emitting), coumarin 6 (C6, green emitting) or Nile red (red emitting), and employing Mg:Ag as cathode have been characterized previously. Here, we fabri-

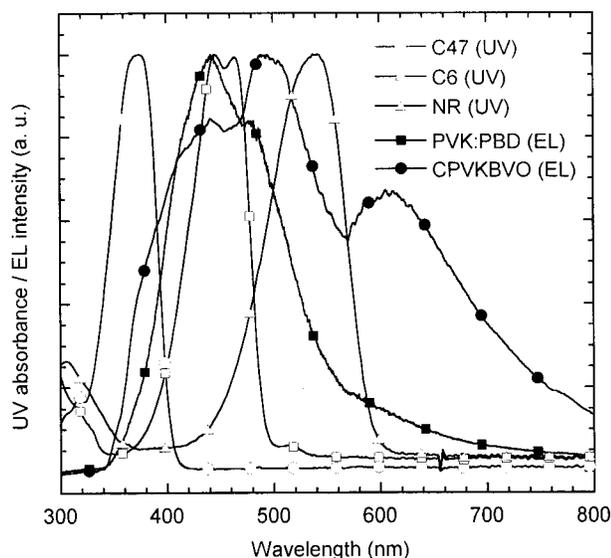


FIG. 7. UV-vis absorption spectra of coumarin 47 [C47(UV)], coumarin 6 [C6(UV)], and nile red [NR(UV)] superimposed on the EL spectra obtained from ITO/PVK:PBD(71:29)/Ca and ITO/CPVKBVO($w_1=0.70$)/Ca devices at 20 V.

cate similar devices with Ca as the cathode and compare all four sets of data (two matrices \times two cathode types) to elucidate the effect of excited-state complex formation on device performance.

Table I summarizes the efficiencies and brightnesses of the dye-doped devices. The efficiencies of the Ca devices are lower than those of the Mg:Ag devices because the dye doping level, and the ratio of carbazole to oxadiazole groups in the blend and copolymer, were optimized⁵ for the Mg:Ag cathode; ease of carrier injection, which is strongly affected by the electrode type, also affects the balance between carriers. However, the same trends are seen with both electrode types: among the three dye-doped PVK:PBD LEDs, the C6 device has the highest efficiency, while among the CPVKBVO copolymer LEDs, that doped with NR has the highest efficiency. (The lower brightnesses for copolymer devices doped with NR versus C6 result from the lower sensitivity of the human eye to orange versus green emission.)

Two classes of excitation mechanism are possible in EL: energy transfer (by Förster or Dexter mechanisms) and charge trapping, and often both are operative in a single device.^{12,44} Since photoexcitation does not normally generate free carriers, PL emission from dilute dyes can result from energy transfer only. PL spectra of dye-doped PVK and PVK:PBD blends indicate very efficient energy transfer, such that <1 wt % dye doping yields emission almost entirely from the dye.⁵ Recently, experiments on PVK:PBD doped simultaneously with two dyes have revealed the importance of charge trapping as well.⁴⁵ We thus consider that both mechanisms are operative in our devices. However, the energy levels of the carbazole and oxadiazole units are not likely to change significantly when incorporated into a polymer (as they are not conjugated to the connecting units), so the efficiency of charge trapping should be essentially the same in both blend and copolymer devices, leaving differences in energy transfer efficiency as the origin of the difference in the optimum dopant for the blend versus copolymer matrices.

The difference in optimum dopant for the different matrices³⁰ can be understood with reference to Förster energy transfer theory. Though originally developed⁴⁶ to describe long-range energy transfer between molecular excited states, we consider here that such transfer should also be possible from more delocalized (bimolecular) excited states such as exciplexes and electroplexes. Figure 7 shows the UV-vis absorption spectra of C47, C6, and NR superimposed on the EL spectra of PVK:PBD (71:29) and CPVKBVO ($w_1=0.70$). Among the three dyes, C6 has the best absorption overlap with the EL spectrum of the PVK:PBD blend, while NR has the best absorption overlap with the EL spectrum of the copolymer. Thus, the PVK:PBD matrix should transfer energy most efficiently to the C6 dye, while the copolymer will transfer energy most efficiently to NR. C47 has poor absorption overlap with the EL spectra of both the blend and copolymer accounting for the poorer efficiencies across the board for devices doped with C47.

The differences in energy transfer efficiency also manifest themselves directly in the EL spectra, when devices fabricated with the same dye but different matrices are com-

TABLE I. Device performance figures.

Emissive layer			Mg-Ag cathode			Ca cathode		
Dye	Dye level (wt %)	Matrix	External quantum efficiency (%) ^a	Brightness (cd/m ²)	Current density (mA/cm ²)	External quantum efficiency (%) ^a	Brightness (cd/m ²)	Current density (mA/cm ²)
C47	0.65	PVK:PBD ^b	0.5 ^d	110	25	0.1	150	300
C6	0.3	PVK:PBD ^b	1.1 ^d	650	25	0.4	2750	300
NR	0.16	PVK:PBD ^b	0.3	105	25	0.3	1780	300
C47	0.65	CPVKBVO ^c	0.1 ^e	8.4	50	0.03	40	300
C6	0.3	CPVKBVO ^c	0.2 ^e	160	50	0.04	210	300
NR	0.16	CPVKBVO ^c	0.4 ^e	105	50	0.06	100	300

^aMaximum value, although variation over operating range is modest, see data in Refs. 5 and 14.

^bWeight ratio 71:29 PVK:PBD.

^cWeight ratio 70:30 NVK:BVO.

^dFrom Ref. 5.

^eFrom Ref. 14.

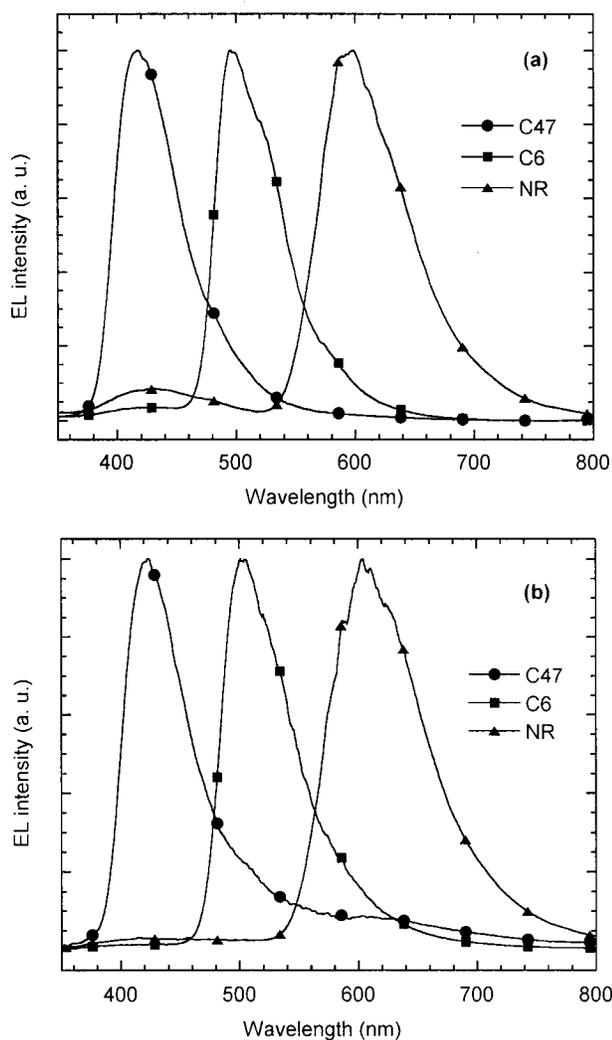


FIG. 8. EL spectra of (a) ITO/PVK:PBD(71:29):dye/Ca and (b) ITO/CPVKBVO($w_1=0.70$):dye/Ca devices, where the dye is C47 (0.65 wt %), C6 (0.3 wt %), or NR (0.16 wt %).

pared. Figures 8(a) and 8(b) show the EL spectra of dye-doped PVK:PBD (71:29) and CPVKBVO ($w_1=0.70$) devices, respectively, all with Ca cathodes. For the C47-doped devices, the especially poor energy transfer to the dye from the CPVKBVO matrix is evident in Fig. 8(b) by the presence of a residual maximum at 610 nm due to PVK electroluminescence, absent in the analogous PVK:PBD:C47 device whose spectrum is shown in Fig. 8(a). For the C6-doped devices, little emission from the matrix is seen in either case, implying efficient energy transfer from either the blend or copolymer matrix to C6. Finally, for the NR-doped devices, the opposite matrix effect is seen from the C47-doped devices: the EL spectrum of the PVK:PBD:NR device [Fig. 8(a)] clearly shows emission from the PVK:PBD matrix, peaking at 435 nm, which is absent in the spectrum from the analogous CPVKBVO:NR device [Fig. 8(b)]. Residual matrix emission can also be seen in the data of Johnson *et al.*³⁰ for PVK:PBD blend devices doped with dyes which, like NR, had absorption spectra too far to the red to overlap well with the PVK:PBD emission spectrum. This demonstrates the substantial effect that excited-state complexes can

have on device performance: although the active moieties (carbazole and oxadiazole) are identical for the blend and copolymer matrices, the different excited state complexes in the two cases (blend exciplex emitting at 440 nm versus copolymer electroplex emitting at 500 nm) directly affect the ability to transfer energy to the emitter dye.

IV. CONCLUSIONS

Excited-state complexes are formed in PVK:PBD blends, as well as in copolymers containing carbazole and oxadiazole moieties in the side chains. In the blends, these complexes are conventional exciplexes, whose emission is visible in both PL and EL. In the copolymers, however, the emission is visible only in the EL spectrum, indicating that these complexes are electroplexes (electron-hole heteropairs); exciplex formation is suppressed in the copolymer by the topological constraints imposed on the carbazole and oxadiazole groups by their connection to the polymer backbone. The presence of excited-state complexes creates additional peaks in the EL spectrum which are significantly redshifted from the EL of the PVK homopolymer, but by different amounts for the blends (exciplexes, 30 nm shift of main peak plus shoulder shifted by 70 nm) and the copolymers (electroplexes, 90 nm shift). These differences impact the quantum efficiencies and brightnesses of dye-doped LEDs made from the two matrices, since the extent of overlap between the matrix EL spectrum and the dye absorption spectrum influence the efficiency of Förster energy transfer. Moreover, these shifts suggest that the dopant yielding the most efficient device can differ between the blend and analogous copolymer matrices, as well as from the pure PVK homopolymer matrix. For the blend matrix, C6 was found to be the best dopant of the three dyes examined, while NR was optimal for the copolymer matrix.

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