

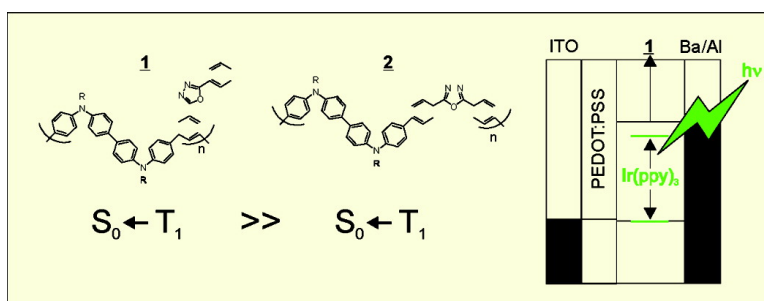
Article

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Carbazole Compounds as Host Materials for Triplet Emitters in Organic Light-Emitting Diodes: Polymer Hosts for High-Efficiency Light-Emitting Diodes

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Abstract: A carbazole homopolymer and carbazole copolymers based on 9,9'-dialkyl-[3,3']-bicarbazolyl, 2,5-diphenyl-[1,3,4]-oxadiazole and 9,9-bis(4-[3,7-dimethyloctyloxy]phenyl)fluorene were synthesized and their electrical and photophysical properties were characterized with respect to their application as host in phosphorescent polymer light-emitting diodes. It is shown that the triplet energy of a polymer depends on the specific connections between its building blocks. Without changing the composition of the polymer, its triplet energy can be increased from 2.3 to 2.6 eV by changing the way in which the different building blocks are coupled together. For poly(9-vinylcarbazole) (PVK), a carbazole polymer often used as host for high-energy triplet emitters in polymer light-emitting diodes, a large hole-injection barrier of about 1 eV exists due to the low-lying HOMO level of PVK. For all carbazole polymers presented here, the HOMO levels are much closer to the Fermi level of a commonly used anode such as ITO and/or a commonly used hole-injection layer such as PEDOT:PSS. This makes high current densities and consequently high luminance levels possible at moderate applied voltages in polymer light-emitting diodes. A double-layer polymer light-emitting diode is constructed comprising a PEDOT:PSS layer as hole-injection layer and a carbazole-oxadiazole copolymer doped with a green triplet emitter as emissive layer that shows an efficacy of 23 cd/A independent of current density and light output.

Introduction

At the moment, much attention is being directed to organic light-emitting diodes (OLEDs) for display applications. These devices are either based on small molecules (small molecule OLEDs) or on polymers (PLEDs). Small molecule OLEDs are prepared by the consecutive vacuum-evaporation of several organic layers, where each layer fulfils a specific function such as charge injection, charge transport, or emission of light. By optimizing the properties of these layers, highly efficient small molecule OLEDs have been prepared.

Record efficiencies have been obtained by using transition metal complexes as emissive species.^{1–10} Because of strong

spin-orbit coupling in such complexes, intersystem crossing is very efficient leading to an emissive state with high triplet content. Therefore, these transition metal complexes are often referred to as triplet emitters. For small molecule OLEDs simple spin statistics seem to hold, which predict a singlet:triplet ratio of 1:3.^{11,12} In a device without triplet emitters only the singlet excitons can recombine radiatively. Consequently, such a device has a maximal internal efficiency of 25%. When triplet emitters are used in a device, the maximal internal efficiency can be as high as 100% since the triplet emitters can harvest both singlet and triplet excitons.¹³ Although it is still under debate whether

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the singlet–triplet ratio in PLEDs is also 1:3,^{14–19} the possibility of harvesting triplet excitons will be very important for the efficiency of these devices as well.

PLEDs are prepared from solution, either by spin coating (for monochrome devices) or via inkjet printing (for full-color devices). The ease of processability is a strong asset of PLEDs. However, processing from solution does not lend itself easily to the construction of multilayer devices. This means that functions such as charge injection, charge transport, and emission of light, which can be separated in different layers for small molecule OLEDs, have to be integrated into one layer for PLEDs. An exception is the use of a layer of poly-(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (PEDOT:PSS). This layer is applied from aqueous solution and as it is insoluble in organic solvents, a layer of a light-emitting polymer can be applied on top. The PEDOT:PSS layer serves to planarize the indium–tin oxide (ITO) anode and to enable a better and more reproducible injection of holes.

For the use of high-energy (i.e., green or blue light-emitting) triplet emitters it is very important that triplet excitons should not be transferred from the triplet emitter to its host material. This requirement means that the triplet energy of the host should be higher than that of the triplet emitter (see Figure 1). Frequently used polymers such as poly(*p*-phenylenevinylene) (PPV) or poly(fluorene) (PF) have a maximum triplet energy of 1.6 and 2.4 eV respectively, which limits their application as host polymers for triplet emitters to red or yellow triplet emitters. It is not straightforward to find a suitable host for high-energy triplet emitters. Materials with a large HOMO–LUMO energy gap will automatically have a high triplet energy. However, these materials will also suffer from charge injection problems due to misalignment of the HOMO and/or LUMO level with the Fermi levels of the electrodes (or charge injection layers). This problem is more important for a PLED than for a small molecule OLED as the latter benefits from its multilayer device layout, which allows for dedicated charge injection layers for both charge carriers.

It is a real challenge to prepare a polymer that has a high triplet energy and at the same time suitable HOMO and LUMO levels for efficient charge injection. The goal is to have a polymer with a HOMO level at about -5 eV (as the work function of the hole injection layer, PEDOT:PSS, is 4.9 eV), a triplet energy of at least 2.5 eV (to be able to host a green triplet emitter), and a LUMO level at about -2 eV (to enable efficient injection of electrons from commonly used cathodes). These specifications imply that the singlet–triplet energy difference (or exchange energy) of such a polymer should not exceed 0.5 eV, which is a difficult requirement as for most π -conjugated molecules and polymers the exchange energy is larger than 0.5 eV.²⁰ For instance, for PPV and PF the exchange energy is 0.7–0.8 eV.^{21,22}

A well-known polymer that has a high triplet energy is poly-(9-vinylcarbazole) (PVK). This polymer has often been used as host for triplet emitters.^{23–28} However, PVK has a HOMO level at about -5.9 eV, and consequently, a large barrier for injection of holes from PEDOT:PSS, which translates into a low luminance and a high onset voltage. Furthermore, PVK is a unipolar conductor that transports holes only. As a result, an electron conductor has to be admixed to PVK in order to get efficient devices.^{25,26}

In a previous paper, we have shown that coupling two carbazole units via their 3 (3') positions results in a remarkably different behavior as compared to connecting them via their 9 (nitrogen) positions.²⁹ Oligomers in which the carbazoles are coupled via their 3 (3') positions exhibit reversible oxidative behavior, and their HOMO levels can be tailored to match the Fermi levels of commonly used hole injection layers for small molecule OLEDs and/or PLEDs. Most importantly, upon oligomerization the carbazoles maintain a sufficiently high triplet energy to function as host for blue triplet emitters. The work presented here is aimed to transferring the properties of high triplet energy, excellent redox stability and suitable injecting contacts from oligomers to polymers and for this purpose a series of polymers based on 9,9'-dialkyl-[3,3']-bicarbazolyl was synthesized. For each polymer, photo- and electroluminescence measurements, electrical measurements (voltage–current–light scans using a PLED) and cyclic voltammetry measurements were performed. At room temperature, photoluminescence measurements show singlet emission only, while at low temperatures also triplet emission is measured.

In the first part of this paper, the carbazole homopolymer will be described and used to illustrate the functioning of this polymer as host material in a PLED. In the second part, the concept is extended to carbazole-based copolymers containing electron-transporting units to improve charge balance. The series contains various copolymers, that can be divided into three subseries: (a) carbazole–oxadiazole copolymers (see Table 2), (b), carbazole–fluorene copolymers (see Table 3), and (c) carbazole–oxadiazole–fluorene copolymers (see Table 4).

Experimental Section

Materials. The synthesis of the building blocks for the polymers 1–10 has been described in detail elsewhere.²⁹ The synthesis of the polymers (TNO Industrial Technology) will be published in greater detail elsewhere,³⁰ in short: a mixture of 0.5 mmol bisboronic ester derivative(s) and 0.5 mmol dibromo derivative(s) in 25 mL toluene was allowed to stir at room temperature till complete dissolution. Upon deaeration and blanketing with argon, 2 mol % of tetrakis(triphenylphosphine)palladium(0) was added, after which 1.7 mL 20 wt %

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aqueous tetraethylammonium hydroxide was added. The mixture was allowed to reflux during 20 h. Then 1.0 mmol of 4,4,5,5-tetramethyl-1,3,2-dioxaborolylbenzene (end capping reagent) and some fresh catalyst were added, followed by refluxing for another 16 h. The reaction mixture was allowed to cool to room temperature. Several washing steps with aqueous sodium cyanide were performed to remove catalyst residues. Afterward, the organic layer was dried and concentrated. The polymer was isolated after several fractionations respectively precipitations, using tetrahydrofuran and methanol. Yield: ~70% of polymer as fibers. The polymers were characterized with ^1H NMR, SEC, and ICP-MS. ^1H NMR: polymer compositions are comparable with the monomer feed ratios. SEC: molecular weight averages 40–50 kg/mol, with polydispersity 3 typically. ICP-MS: Br < 15 ppm, Pd < 15 ppm.

The green light-emitting transition metal complex fac-tris[2-(2-pyridinyl-kN)(5-(3,4-bis(2-methylpropyloxy)phenyl) phenyl)-kC]-iridium(III) (Covion Organic Semiconductors GmbH) was used as triplet emitter in the PLEDs.³¹ In the remainder of this text, this triplet emitter will be referred to as Ir-SC4.

Polymer Light-Emitting Diodes. PLEDs were fabricated³² under clean room conditions in a nitrogen atmosphere inside a glovebox ($[\text{O}_2]$, $[\text{H}_2\text{O}] < 1$ ppm) using pre-cleaned indium-tin oxide (ITO) coated glass substrates. The ITO was treated in a UV/O₃ photoreactor and remaining dust particles were blown away with ionized nitrogen.

As first layer in the devices a layer of poly(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (PEDOT:PSS, 1:6 dispersion in water, electronic grade AI4083, HC Starck^{33,34}) is used (100 nm). PEDOT:PSS layers were annealed at 180 °C for 2 min. Polymer solutions in chlorobenzene were filtered through a 5- μm filter and spin-coated on top of the PEDOT:PSS layer using a BLE Delta 20 BM spin coater. Metal cathodes were applied by vacuum evaporation through a mask and consisted of either Au or Ba/Al (5 nm Ba capped with 100 nm Al).

The LEDs were characterized by a low-noise single-channel DC power source that can act as a voltage source or current source and as a voltage meter or current meter (Keithley 2400, Keithley Instruments). In a typical characterization of an LED, the voltage is increased stepwise from zero to a preset positive voltage, back to low voltage and ultimately to negative voltage. Light from the diode is coupled into a photodiode and read out by an electrometer/high resistance meter (Keithley 6517, Keithley Instruments). Calibration of the photodiode was done with a luminance meter (Minolta LS-110). In the setup used, light can be detected above a level of about 0.05 cd/m². For recording, the electroluminescence spectra a fiber-coupled spectrograph/CCD camera combination (Ocean Optics S2000) was used. The emission was corrected for the wavelength dependence of the spectrometer.

Fluorescence. Steady-state fluorescence spectra were measured in ambient atmosphere at room temperature in a 90 degree configuration using a Perkin-Elmer LS 50B spectrometer. Spectra of light-emitting polymer layers were measured on plain glass substrates. Spectra of light-emitting polymer solutions were measured using 1 mm quartz cuvettes. The excitation wavelength was 310 nm (4.0 eV). The emission spectra were corrected for the spectral response of the emission monochromator and the photomultiplier tube.

Phosphorescence. The triplet energies were obtained as the maximum of the first vibronic mode ($S_0^{v=0} \leftarrow T_1^{v=0}$) of the corresponding phosphorescence spectra, which are obtained after photoexciting the singlet manifold followed by intersystem crossing to the triplet manifold. Thin film samples were attached to the coldfinger of a displex helium cryostat ($T < 20$ K) and excited by a 150 ps pulsed Nd:YAG laser at

355 nm (3.5 eV). The spectrally dispersed luminescence of the film was focused onto a gated intensified CCD camera, which allowed rejection of the strong prompt fluorescence before the detection of the comparably weak phosphorescence started. A detailed description of the employed experimental setup is given elsewhere.³⁵

Cyclic Voltammetry. Cyclic voltammetry measurements were recorded in dichloromethane, with 1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte (scan rate of 100 mV/s). The working electrode was a platinum disk (0.2 cm²), the counter electrode was a platinum plate (0.5 cm²), and a saturated Ag/AgCl reference electrode (having a potential of 0.2 V versus NHE) was used. No reduction wave has been observed down to about -2.0 V. All polymers showed reversible oxidative behavior. The oxidation potentials were measured as the potential at half-height of the oxidation wave (half-wave oxidation potential, or $E_{1/2}$). The measured oxidation potentials can be converted into ionization potentials by relating the electrochemical energy scale (with respect to NHE) to the vacuum energy scale. At room temperature, the Fermi level of NHE is -4.5 eV with respect to the vacuum level,³⁶ which means that the ionization potential (IP) can be calculated using $\text{IP [eV]} = 4.7 + E_{1/2}$. The ionization potential can be taken as a measure for the energy of the highest occupied molecular orbital (HOMO).

Results and Discussion

Carbazole Homopolymer. The chemical structure of the carbazole homopolymer (**1**) is shown in Figure 1, together with a schematic energy level diagram. For a standard PLED containing a layer of the carbazole homopolymer, a schematic representation of the relevant electronic levels of the various layers is also shown in Figure 1.

For the carbazole homopolymer, the singlet photoluminescence spectra of both the solution and the layer consist of a broad emission band exhibiting vibronic structure (see Figure 2). The spectrum of the polymer layer is slightly shifted to lower energy with respect to that of the polymer solution. For a layer of the carbazole homopolymer, the onset of absorption is at 3.2 eV and the highest-energy vibronic subband of the singlet emission spectrum is centered at 3.0 eV. The former is taken here as measure for the HOMO-LUMO energy difference, and the latter for the singlet energy. In the electroluminescence spectrum, in addition to the broad emission band a second emission band at lower energy is visible (see Figure 2). The intensity of this low-energy emission band depends on the device processing conditions: it increases as the solubility of the polymer in the solvent used for spin-coating decreases. Apparently, the broad emission band is related to the morphology of the polymer layer. This observation, in combination with the fact that the low-energy emission band is only visible in electroluminescence, strongly suggests that the low-energy emission is due to the formation of electromers (see also below).^{37–39}

The triplet emission spectrum of the carbazole homopolymer is recorded at low temperature ($T < 20$ K). Similar as for the singlet emission spectrum, the triplet emission spectrum consists of a broad emission band exhibiting vibronic structure (see

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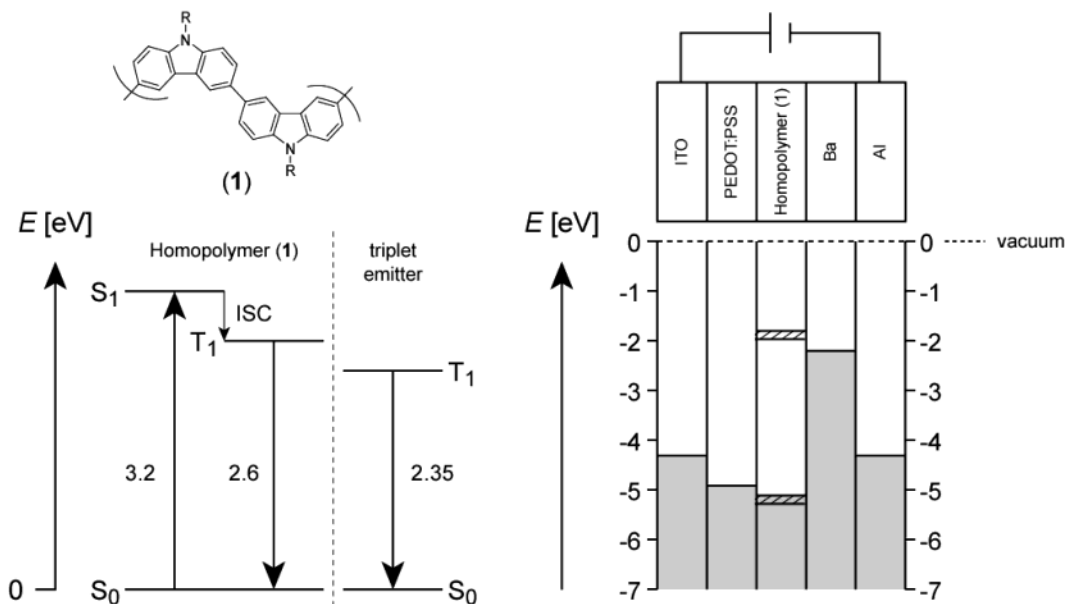


Figure 1. On the left, the chemical structure of the carbazole homopolymer (**1**) is shown, together with a schematic energy level diagram containing the singlet ground state (S_0), the lowest excited singlet state (S_1), and the lowest excited triplet state (T_1). Here, ISC indicates the intersystem crossing transition. The energy level diagram also shows the energy levels of the triplet emitter used in this report. On the right, the layout of an electroluminescent device containing a layer of the carbazole homopolymer is shown. For each layer of the device, the energetic positions of the Fermi level and/or HOMO–LUMO levels are shown relative to the vacuum level. The hatched area indicates the differences in the position of the energy levels as measured by the CV and UPS method.

Figure 3). The spectral shape of the triplet emission spectrum does not depend on the excitation intensity.

The highest-energy triplet vibronic subband of the homopolymer is centered at 2.6 eV which is taken as measure for the homopolymer triplet energy. This triplet energy is significantly higher than that of poly(fluorene)s (2.2–2.4 eV)²² and poly(*p*-phenylenevinylene)s (1.3–1.6 eV),²² the most commonly used polymers in PLEDs, and lower than that of PVK (~ 3 eV). In fact, the triplet energy of the carbazole homopolymer (**1**) matches that of 4,4'-bis(9-carbazolyl)-biphenyl (CBP) which has a triplet energy of 2.56 eV and which is a prominent host for triplet emitters in small molecule OLEDs.

Important parameters for PLEDs are the positions of the HOMO and LUMO levels of the polymer. Contrary to small molecule OLEDs no extra charge injection layers are used so that the HOMO and LUMO levels of the polymer have to be close to the Fermi levels of the anode and cathode, respectively. A measure for the HOMO level is the ionization potential. For all polymers described in this report, the ionization potential is calculated from the half-wave oxidation potential ($E_{1/2}$) as measured by cyclic voltammetry (CV). For a few of these polymers, the ionization potential is also determined from ultraviolet photoelectron spectroscopy (UPS). The results from the CV measurements are used to compare the polymers among each other. The results from the UPS measurements can be used to compare the ionization potentials of the polymers to the work functions of the charge injection contacts (i.e., ITO/PEDOT:PSS, and Ba/Al cathode), as the latter have also been determined with UPS.

From CV measurements, the HOMO level of the carbazole homopolymer (**1**) is calculated to be at -5.3 eV, while UPS yields a value of -5.1 eV. This means that the HOMO level of the carbazole homopolymer is relatively close to the Fermi level of PEDOT:PSS (-4.9 eV), resulting in a good hole injection contact. This is a major improvement with respect to PVK,

where a hole injection barrier of about 1 eV exists at the PEDOT:PSS/PVK interface.

The position of the LUMO level is more difficult to determine. In CV measurements, no reduction wave is observed up to -2.0 V (which means that the LUMO level has to be positioned above -2.7 eV). From the position of the HOMO level (-5.1 eV as determined from UPS) and the onset of absorption (3.2 eV) one can deduce that the LUMO level of the carbazole homopolymer must be positioned at about -2 eV. This represents a small barrier for electron injection from a commonly used cathode such as barium, which has a work function of 2.2 eV (this value might be somewhat different for a stack of barium/aluminum (Ba/Al) as cathode).

To study the charge transport properties of the homopolymer in PLEDs bipolar and unipolar devices were fabricated. Both device types had PEDOT:PSS as hole injecting contact. In bipolar devices, Ba/Al was used as the cathode so that both holes and electrons can be injected into the device. In unipolar devices, gold was used as the cathode, which results in a large barrier for electron injection into the LUMO of the homopolymer and consequently only holes can be injected into the device. The current–voltage characteristics of a bipolar PLED containing a layer of the pristine carbazole homopolymer (shown in Figure 4) are very close to those of unipolar devices. This indicates that holes are the majority charge carriers in devices employing the carbazole homopolymer. This situation is similar to that of PVK, which is a well-known hole transporter but has very poor electron transporting capabilities.⁴⁰

For a bipolar device containing a layer of the carbazole homopolymer, the onset of electroluminescence is at about 3 V, which is close to the HOMO–LUMO energy gap of the carbazole homopolymer, and at 5 V the current density is 10 A/m². However, with about 0.2 cd/A the efficiency of the device

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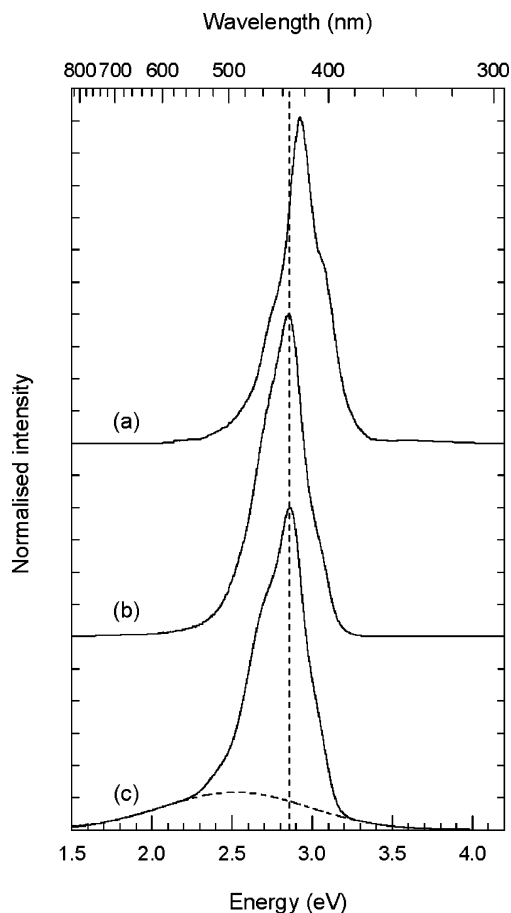


Figure 2. Photoluminescence spectra of the carbazole homopolymer (**1**) in solution (a), and as a polymer layer on glass (b). Both photoluminescence spectra were obtained upon excitation with 4.0 eV. Electroluminescence spectrum of the carbazole homopolymer in a PLED (c). The dashed line in (c) indicates the low-energy emission band that is only visible in electroluminescence. The dashed vertical line is included as an aid for comparison purposes.

is very low. This is a direct consequence of the fact that the carbazole homopolymer is predominantly a hole-transporting polymer resulting in a recombination zone that is located close to the cathode interface, which is detrimental for the efficiency of radiative recombination of excitons.^{41,42}

The polymers described in this paper are specifically designed to function as hosts for a triplet emitter, and not as emitters themselves. The presence of a dopant such as a triplet emitter can significantly influence the electrical and emissive properties of the device. To test the polymers, the green light-emitting iridium complex Ir-SC4 was used. The emission from this triplet emitter has a maximum intensity at 2.35 eV (527 nm). The emitter was molecularly dispersed in the carbazole homopolymer at a mass ratio of 8%. Assuming a uniform distribution, the number density is about $4 \times 10^{19} \text{ cm}^{-3}$, corresponding to a mean intermolecular distance of about 30 Å. At this distance, concentration quenching due to dipolar coupling among the metal complexes slightly reduces the luminescence quantum yield to 80–90% of its low concentration limit of ca. 0.4 (mass ratio < 1%, corresponding to a mean intermolecular distance of 46 Å). In a PLED, the electro-

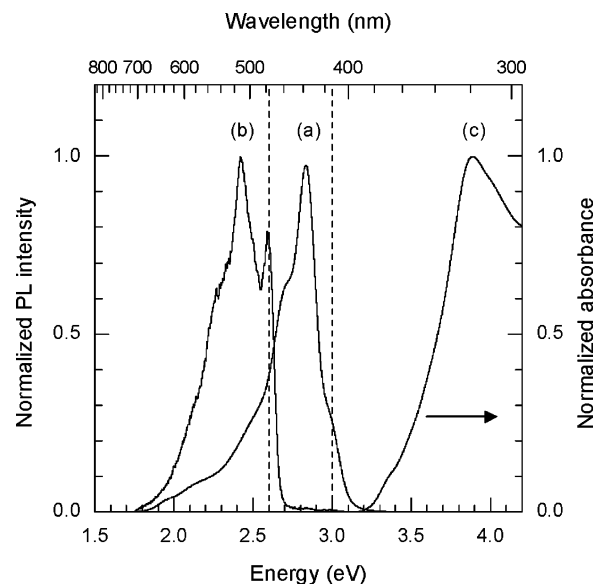


Figure 3. Singlet (a) and triplet (b) photoluminescence spectra of a layer of the carbazole homopolymer (**1**) on glass, obtained at $T < 20 \text{ K}$ upon excitation with 3.5 eV. The room-temperature absorption spectrum of the carbazole homopolymer is represented by (c). The vertical dashed lines indicate the position of the highest-energy vibronic subbands. These positions are taken as measure for the singlet and triplet energies of the carbazole homopolymer (3.0 and 2.6 eV, respectively).

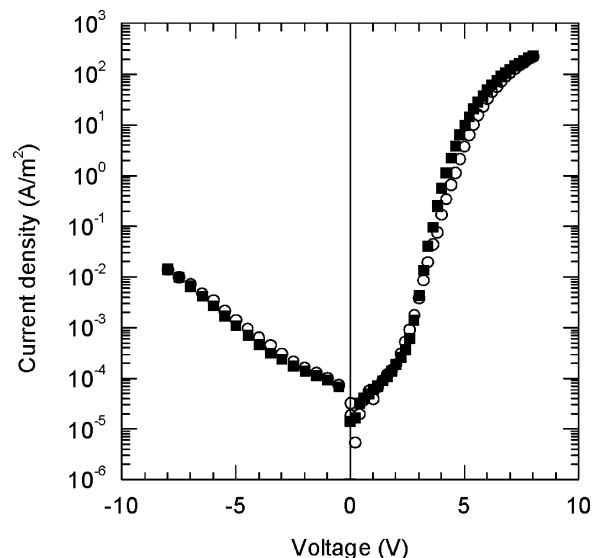


Figure 4. Current density as a function of applied voltage for bipolar PLEDs containing a layer of the pristine carbazole homopolymer (**1**) (open circles) and a layer of the homopolymer into which the triplet emitter is dispersed at a mass ratio of 8% (solid squares).

luminescence of the carbazole homopolymer host is completely quenched and only emission from the triplet emitter is observed (see Figure 5).

When the triplet emitter is dispersed in the homopolymer, the current–voltage characteristics do not change (see Figure 4). From CV measurements, the half-wave oxidation potential of the triplet emitter is determined to be 0.7 V.

From CV measurements (see Table 1), it is clear that the oxidation potential of the triplet emitter is larger than that of the carbazole homopolymer. This means that when this triplet emitter is dispersed in the carbazole homopolymer, it does not act as a trap for holes, which are the majority charge carriers in devices based on the carbazole homopolymer. Consequently,

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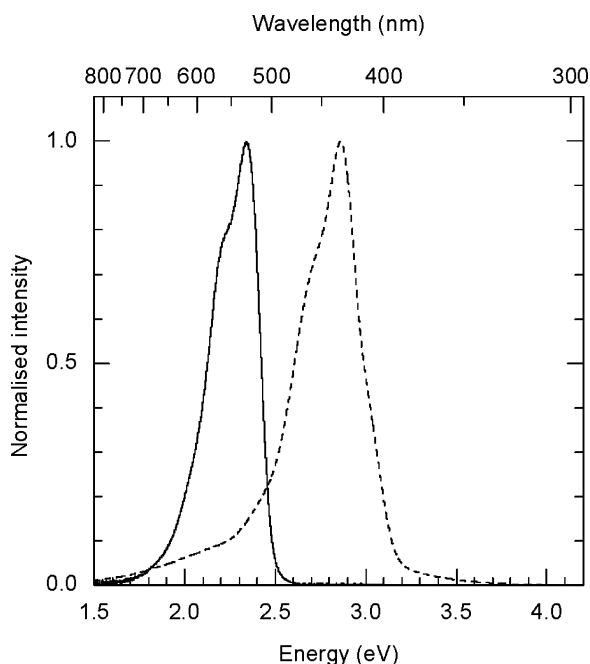
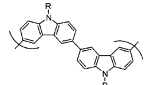
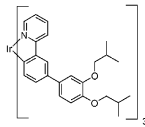


Figure 5. Electroluminescence spectrum of a PLED containing a layer of the carbazole homopolymer (**1**) into which the triplet emitter Ir-SC4 is dispersed at a mass ratio of 8% (solid line). For comparison purposes, the electroluminescence spectrum of a PLED containing the pristine carbazole homopolymer is shown with a dashed line.

Table 1. Chemical Structure, Half-Wave Oxidation Potential (versus saturated Ag/AgCl), Onset of Absorption and Energy of the Triplet Emission ($S_0 \leftarrow T_1$), for the Homopolymer and the Triplet Emitter

	Structure	$E_{1/2}$ [V]	Abs. E_{onset} [eV]	$S_0 \leftarrow T_1$ E [eV]
1.		0.55	3.2	2.60
Ir-SC4		0.74	2.37*	2.35

*Metal to ligand charge transfer (MLCT) transition.

the current density is not significantly influenced by the presence of the triplet emitter. The efficiency of the doped homopolymer increases slightly compared to the pristine homopolymer, but not beyond 0.4 cd/A. So, although the luminescence quantum yield of the triplet emitter is still 0.32–0.36 at the concentration employed in the device (see above), and the carbazole homopolymer has a suitable triplet energy and no large barrier for hole injection, the homopolymer apparently is not a suitable host for the particular triplet emitter used here. Similarly as for the pristine carbazole homopolymer, for the doped carbazole homopolymer the low efficiency probably results from charge carrier imbalance and the fact that the recombination zone is close to the cathode interface. By shifting the recombination zone away from the cathode interface, the efficiency should increase. One method for testing this assumption is by inserting an organic hole- and exciton-blocking, electron-transporting

layer between the emissive polymer layer and the cathode (see Figure 6). A suitable material for such a layer is 1,3,5-tris-(phenyl-2-benzimidazole)-benzene (TPBI), which can be vacuum-evaporated on top of the polymer layer previous to vacuum-evaporation of the cathode. TPBI has a very low-lying HOMO level at -6.2 eV (hence its hole-blocking capabilities) and a large HOMO–LUMO energy difference of 3.4 eV (hence its exciton-blocking capabilities).^{43–47} When a 30 nm layer of TPBI is inserted between the carbazole homopolymer layer (into which the triplet emitter is dispersed) and the cathode, the efficiency increases considerably from about 0.4 cd/A to 15 cd/A (see Figure 6).

It is also important to point out that the efficiency is independent of the current density. Neither triplet–triplet annihilation nor scattering of triplet excitons and charge carriers diminish the number of excited states. Apparently, the triplet excitons are rather immobile during their lifetime (~ 1.5 μs). This could also be deduced from the only slightly decreased luminescence quantum yield due to self-quenching by dipolar coupling of the triplet emitter at the mass ratios of 8% employed in the PLEDs (see above). However, in the multilayer device part of the applied voltage drops over the TPBI layer and the positive charge carriers are blocked from reaching the cathode. Consequently, the current density in the light-emitting layer at a certain applied voltage has decreased by about a factor of 2 in comparison to the device without a TPBI layer.

Since in the systems studied here the triplet excitons are rather immobile, an exciton blocking layer is not required and the main function of the TPBI layer is to improve charge carrier balance by blocking the majority charge carriers (i.e., holes). The recombination takes place at the interface of the doped homopolymer layer and the TPBI layer and thereby the recombination zone is separated from the cathode.

An alternative method for improving the charge carrier balance and shifting the emission zone away from the cathode interface is to incorporate electron-transporting moieties into the polymer backbone. With this concept, the charge carrier balance is improved by increasing the density of minority charge carriers. This method to improve charge carrier balance is preferred over the method of blocking the majority charge carriers since it enables higher current densities and consequently higher luminance levels at lower voltages (i.e., the power efficiency of the device is increased). Furthermore, this approach allows for a simpler and hence cheaper device architecture since no extra blocking layers have to be inserted between the emissive polymer and the cathode.

Copolymers. Suitable electron-transporting moieties are for instance oxadiazole derivatives, that are well-known for improving the charge balance in several copolymers.^{39,48–51} In a previous

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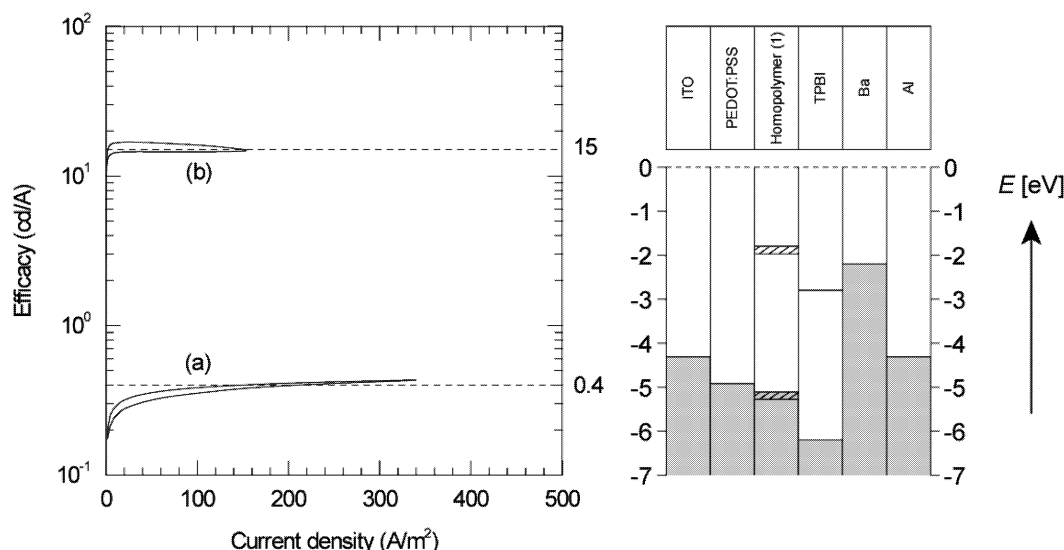


Figure 6. Efficacy as a function of current density for doped PLEDs containing a layer (80 nm) of the carbazole homopolymer (**1**). Graph (a) represents a device containing only a layer of the carbazole homopolymer, while graph (b) represents a device with an additional layer of TPBI (30 nm) between the homopolymer layer and the cathode. On the right, the device architecture and a schematic representation of the electronic levels is shown. Both devices have ITO covered with a layer (100 nm) of PEDOT:PSS as anode, and 5 nm Ba covered with 100 nm Al as cathode. The triplet emitter Ir–SC4 is dispersed in the homopolymer layer at a mass ratio of 8%. The hatched area indicates the differences of the position in the energy levels as measured by the CV and UPS method.

Table 2. Chemical Structure, Half-Wave Oxidation Potential (versus saturated Ag/AgCl), Onset of Absorption and Energy of the Triplet Emission ($S_0 \leftarrow T_1$), for the Carbazole–Oxadiazole Copolymers

	Structure	$E_{1/2}$ [V]	Abs. $S_0 \leftarrow T_1$	
			E_{onset} [eV]	E [eV]
2.		0.69	2.9	2.32
3.		0.73	3.1	2.57
4.		0.75	3.1	2.56

contribution, we have shown that oxadiazole derivatives can be incorporated into carbazole oligomers without lowering the triplet energy of the oligomer.²⁹ For our experiments, we have used 2,5-diphenyl-[1,3,4]-oxadiazole to make copolymers with 9,9'-dialkyl-[3,3']-bicarbazolyl (see Table 2). Next to oxadiazole, fluorene is also used to improve the charge balance in carbazole-containing polymers.⁵² Therefore, for a second series of copolymers 9,9-bis[4-(3,7-dimethyloctyloxy)phenyl]fluorene was used (see Table 3). Finally, copolymers were synthesized in which both 2,5-diphenyl-[1,3,4]-oxadiazole and 9,9-bis[4-(3,7-dimethyloctyloxy)phenyl]fluorene were used in addition to 9,9'-dialkyl-[3,3']-bicarbazolyl (see Table 4).

The copolymers containing oxadiazole differ in the way in which the oxadiazole derivative is incorporated into the polymer

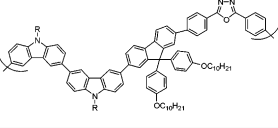
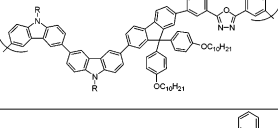
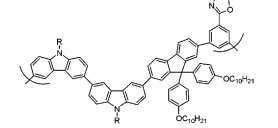
Table 3. Chemical Structure, Half-Wave Oxidation Potential (versus saturated Ag/AgCl), Onset of Absorption and Energy of the Triplet Emission ($S_0 \leftarrow T_1$), for the Carbazole–Fluorene Copolymers

	Structure	$E_{1/2}$ [V]	Abs. $S_0 \leftarrow T_1$	
			E_{onset} [eV]	E [eV]
5.		0.94	3.0	2.29
6.		0.78	3.1	2.31
7.		0.76	3.2	2.6

main chain. First, the oxadiazole can be incorporated with its long axis parallel to the polymer main chain (as for the copolymers **2**, **3**, **8**, and **9**). Of these copolymers, we refer to **2** and **8** as containing a para-coupled oxadiazole, and to **3** and **9** as containing a meta-coupled oxadiazole, where para and meta refer to the coupling pattern at the phenyl rings of the oxadiazole. Second, the oxadiazole can be incorporated with its long axis perpendicular to the polymer main chain (as for the copolymers **4** and **10**), with only one of its phenyl rings being part of the polymer main chain. Fluorene can also be built into the copolymer in two ways. It is either connected to the carbazole via its 2 and 7 positions, which we will refer to as para-coupled fluorene (**5**, **6**, **8**, **9**, **10**), or it is connected via its 3 and 6 positions which we will refer to as meta-coupled fluorene (**7**).

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Table 4. Chemical Structure, Half-Wave Oxidation Potential (versus saturated Ag/AgCl), Onset of Absorption and Energy of the Triplet Emission ($S_0 \leftarrow T_1$), for the Carbazole–Oxadiazole–Fluorene Copolymers

	Structure	$E_{1/2}$ [V]	Abs. E_{onset} [eV]	$S_0 \leftarrow T_1$ E [eV]
8.		0.78	2.95	2.21
9.		0.81	3.1	*
10.		0.82	3.1	2.29

*The triplet emission spectrum of this compound is very weak and does not allow for an accurate determination of the triplet energy and/or lifetime.

It is important that copolymerization does not significantly influence the positions of the HOMO and LUMO levels. For the copolymers, the values for the half-wave oxidation potentials (0.7–0.8 V, see Table 2 to Table 4) are slightly larger than that of the homopolymer (0.6 V, see Table 1), but comparable to that of the triplet emitter (0.74 eV, see Table 1). For the carbazole-oxadiazole copolymer **4**, the ionization potential was also determined with UPS, which yielded a value of 5.1 eV (i.e. similar to that of the carbazole homopolymer). A special case is the carbazole–fluorene copolymer **5** (see Table 3). For this copolymer, a half-wave oxidation potential of 0.94 V is measured, which is markedly larger than that of the other copolymers. The reason for this is that for all copolymers a carbazole dimer is used as building block in the copolymerization along with oxadiazole or fluorene except for copolymer **5** where a carbazole monomer was used as building block. It has been reported before that the ionization potential of the carbazole monomer is significantly larger than that of the carbazole dimer.²⁹ As this behavior is reflected in the copolymer, apparently the oxidative behavior is mainly determined by the carbazole unit in the copolymer. This means that to ensure a low-barrier hole injection contact, a carbazole dimer should be used as building block for the copolymers.

As was mentioned before for the homopolymer, the LUMO levels of the copolymers cannot be measured directly. However, they can be estimated to be positioned between -2.7 eV (a lower limit given by the absence of a reduction wave up to -2 V in CV measurements) and about -2.1 eV (an upper limit given by the absorption onset). This means that for all copolymers the LUMO is close to the Fermi level of the Ba/Al cathode resulting in a barrier-free or low-barrier contact.

Comparable to the homopolymer, the HOMO and LUMO levels of the copolymers are still relatively close to the Fermi levels of the anode (PEDOT:PSS) and cathode (Ba/Al), respectively. In other words, the copolymers represent a good

compromise between a high-band gap material and low-barrier charge injection contacts (see Figure 7).

The excited-state behavior of carbazoles and carbazole derivatives is very complex. A wealth of possible emitting states exists that can be different for singlet and triplet emission⁵³ and also for electro- and photoluminescence. Here, we only present the excited-state features that are relevant for the functioning of the carbazole (co)polymers as hosts in PLEDs. For the copolymers, the photoluminescence and electroluminescence characteristics are similar to those of the homopolymer, including the presence of an additional low-energy emission band in electroluminescence, and its dependence on the solubility of the polymer. Of course, when dealing with copolymers, a greater variety of excited-state complexes can be formed (i.e., not just electromers but also electroplexes³⁹). In carbazole–oxadiazole copolymers where the carbazole and oxadiazole groups are present as side groups, similar low-energy emission bands in electroluminescence have been reported and attributed to electron–hole hetero pairs between oxadiazole and carbazole.⁵⁴ As an electroplex only exists in the excited state (i.e., it has no binding ground state), it is not possible for electroplexes to be directly populated via excited-state energy transfer. This is an important point, as it means that a polymer that exhibits low-energy electroplex emission in its pristine form can still be used as host for a guest that emits at an energy higher than the low-energy electroplex emission of the host polymer.

While the high-energy emission band of the homopolymer shows vibronic structure, for most of the copolymers this emission band is featureless (at room temperature and low temperature), which makes the determination of the singlet energy for the copolymers less straightforward than for the homopolymer. The triplet emission spectrum still shows a clear vibronic structure so that the triplet energy of the copolymers can be accurately determined.

Probably most importantly, it is necessary to have control over the triplet energy when the copolymers are made from their building blocks. In a previous publication, we have shown that for maintaining a high triplet energy it is necessary to limit the length of the longest poly(*p*-phenylene)chain that can be identified in the chemical structure to biphenyl.²⁹ This concept is nicely illustrated by two of the carbazole-fluorene copolymers shown in Table 3. In the copolymer containing para-coupled fluorene (**6**) a *p*-quaterphenyl unit can be identified, and consequently its triplet energy (2.31 eV) is lower than that of the copolymer containing a meta-coupled fluorene (**7**) in which only a biphenyl unit can be identified (2.6 eV). When the copolymer contains a para-coupled fluorene (**5** and **6**), it does not matter for the triplet energy whether 9-alkyl-carbazole (**5**) or 9,9'-dialkyl-[3,3']-bicarbazolyl (**6**) is present next to the fluorene. For such copolymers the triplet exciton is delocalized over the fluorene and two phenyls of neighboring carbazole groups.

From comparing the triplet energies of the carbazole-oxadiazole copolymers in Table 2, it is clear that to limit the delocalization of the triplet exciton, the phenyl ring of the oxadiazole should not be para-substituted. In case of para substitution, a triplet exciton can be delocalized along a larger

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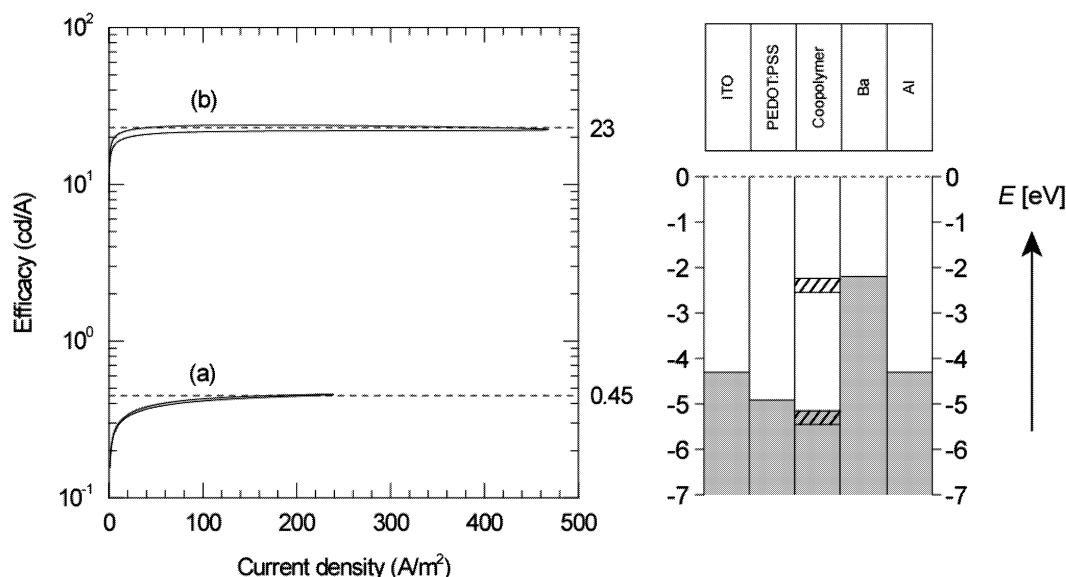


Figure 7. Efficacy as a function of current density for doped PLEDs containing a layer (80 nm) of a carbazole-oxadiazole. Graph (a) represents a device containing a layer of the carbazole-oxadiazole copolymer **2**, while graph (b) represents a device with a layer of the carbazole-oxadiazole copolymer **4**. On the right, the device architecture and a schematic representation of the electronic levels is shown. Both devices have ITO covered with a layer (100 nm) of PEDOT:PSS as anode, and 5 nm Ba covered with 100 nm Al as cathode. The triplet emitter Ir-SC4 is dispersed in the copolymer layer at a mass ratio of 8%. The hedged area indicates the differences in the position of the energy levels as measured by the CV and UPS method.

part of the oxadiazole unit, thereby lowering its energy.^{55,56} For the copolymers with high triplet energies (**3**, **4**, and **7**), the spectral shape and the energy of the triplet emission are similar to that of the carbazole homopolymer (**1**), so it is reasonable to conclude that in these copolymers the triplet exciton is localized on the carbazole part of the polymer main chain.

When comparing the triplet energies from Table 2 and Table 4, it is clear that the carbazole-oxadiazole-fluorene copolymers, **8**, **9**, and **10** all have a lower triplet energy than their corresponding carbazole-oxadiazole copolymers **2** to **4**. The copolymers **8**, **9**, and **10** all have *p*-quaterphenyl as the longest poly(*p*-phenyl) chain and consequently they all have a low triplet energy.

The above-mentioned examples illustrate that control over the triplet level can indeed be achieved to some extent in a copolymer system. Without changing the composition of the polymer, its triplet energy can be tuned by changing the way in which the different monomers are coupled together.

Obviously, the final proof of the applicability of the copolymers as efficient hosts for triplet emitters lies in the construction of a device. Bipolar PLEDs were constructed with a layer of a copolymer sandwiched between an ITO/PEDOT:PSS anode and a Ba/Al cathode. As was the case for the luminescence characteristics (the intensity of the electroplex emission), the current–voltage characteristics are influenced by the solubility and purity of the various polymers, which makes it difficult to observe a clear trend. However, no large differences in current–voltage characteristics are observed for the polymers studied in this report (i.e., for a certain applied voltage about the same amount of current flows through the carbazole homopolymer as through the copolymers). As mentioned before, the copolymers are specifically prepared to improve the charge balance. When no changes are observed in the current–voltage charac-

teristics, this could either mean that despite the efforts the charge balance has not improved at all, or that it has improved but the mobilities and/or injection barriers for holes and electrons have both changed in such a way that the net current–voltage characteristics are unchanged.

To determine whether the charge balance has improved or not, the triplet emitter should be dispersed in each of the copolymers. An improvement of the charge balance will result in a shift of the recombination zone away from the cathode interface, and consequently an increase in efficiency will be observed. As mentioned before, for a triplet emitter to emit efficiently in a host polymer, it is a prerequisite that the triplet energy of the polymer is higher than that of the triplet emitter. When the host polymer has a triplet energy lower than that of the triplet emitter, triplet excitons can be transferred from the triplet emitter to the host polymer where they will recombine nonradiatively. As a result, the emission of the triplet emitter is quenched in these host polymers. This can clearly be seen in Figure 7. Using the copolymer **2** with a triplet energy of 2.32 eV as host for the green light-emitting triplet emitter Ir-SC4 results in low efficiencies of 0.45 cd/A (multilayer devices, i.e., copolymer plus TPBI, gave a low efficiency as well, data not shown). The same holds true for the other copolymers with low triplet energies **5**, **6** and for **8** to **10** (data not shown).

The only polymers that fulfill the prerequisite of having a triplet energy high enough for the green light-emitting triplet emitter Ir-SC4 are **1**, **3**, **4**, and **7**. Figure 7 shows the efficiency of a device with the copolymer **4** as host for the triplet emitter Ir-SC4. The efficiency is independent of current density, and has a mean value of 23 cd/A. Upon comparing the efficiency to that of a device containing the homopolymer **1** (see Figure 6), it is clear that it has drastically increased upon incorporating oxadiazole moieties into the carbazole backbone. Evaporating a blocking layer on top of the doped copolymer **4** does not improve the efficiency considerably. This is a clear indication for an improvement of the charge balance that has resulted in

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a shift of the recombination zone away from the cathode interface. Furthermore, even if the two-layer copolymer device is compared to the multilayer homopolymer device (i.e., homopolymer plus TPBI) the efficiency has increased. This demonstrates that a high-energy triplet emitter when dispersed in a polymer can be made to emit efficiently in a standard two-layer PLED.

Interestingly, the emission of a PLED containing *any* of the polymers **1–10** studied in this report as host for the green light-emitting triplet emitter Ir–SC4 results exclusively from the triplet emitter. The red electroplex emission as observed in devices containing pristine polymers is absent in devices containing doped polymers. The absence of the red emission cannot be accounted for by endothermic energy transfer from the electroplex to the triplet emitter as the energy difference between the electroplex emission and the lowest-energy absorbance of the green triplet emitter is too large to be compensated by thermal excitations. The absence of the red electroplex emission is a consequence of the population of the green triplet emitter. In principle, the triplet emitter can be excited by two different pathways: (1) electrons and holes are sequentially trapped on the emitter and an excited state is directly formed on the triplet emitter, or (2) an excited state is first generated on the polymer and then transferred to the triplet emitter. In our devices, the excitation path is determined by the energetic landscape of the polymer/triplet emitter system. The triplet emitter is no trap for positive charge carriers (see oxidation potential in Table 1 and Table 2) Apparently, in all copolymer systems the triplet emitter acts as trap for electrons: consequently, no excited states are formed on the host polymer but instead the excited states are formed directly on the triplet emitters by sequential trapping of charge carriers (i.e., pathway 1). Since no excited states are formed on the host polymer the electroplexes cannot get populated and consequently no red electroplex emission can be seen.

Conclusion

The simplicity of the device architecture and the ability of solution processing are the most important features of PLEDs,

enabling intrinsically low-cost production techniques for large-area displays. Therefore, distinct functions that can be separated into multiple layers in small molecule OLEDs have to be integrated into the chemical structure of the materials comprising the light-emitting layer in PLEDs. For phosphorescent PLEDs, this means that high efficiencies and luminance levels suitable for practical applications have to be reached without the use of extra charge transport, hole and/or exciton blocking layers. We have demonstrated that this can be achieved with carbazole-oxadiazole copolymers. One of the building blocks is 9,9'-dialkyl-[3,3']-bicarbazolyl, which is built into the main chain of the polymer so that all sites prone to oxidative degradation known in carbazoles are protected. The other building block of a carbazole-oxadiazole copolymer is 2,5-diphenyl-[1,3,4]-oxadiazole, which ensures a sufficient charge carrier balance. In this class of carbazole-oxadiazole copolymers, the delocalization of triplet excitons can be limited so that the copolymer has a triplet energy of about 2.6 eV. This energy is similar to that of commonly used hosts for triplet emitters in small molecule OLEDs. Most importantly, a standard PLED containing a layer of a carbazole-oxadiazole copolymer into which a green light-emitting triplet emitter is molecularly dispersed shows a high efficiency of 23 cd/A which does not decrease at high current densities and high luminance levels.

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Supporting Information Available: Monomers, monomer ratios in the polymers. This materials is available free of charge via the Internet at <http://pubs.acs.org>.

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