Carbazole Compounds as Host Materials for Triplet Emitters in Organic Light-Emitting Diodes: Tuning the HOMO Level without Influencing the Triplet Energy in Small Molecules

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Abstract: A series of novel carbazole compounds was synthesized and tested for their suitability as host for triplet emitters in an organic-light emitting diode (OLED). In these compounds, a carbazole unit is either connected to other carbazole units to form carbazole dimers and trimers or to fluorene and oxadiazole derivatives to form mixed compounds. The HOMO level of carbazole compounds can be tuned by substitution at the 3, 6, and/or 9 positions. Making oligomers by connecting carbazole molecules via their 3 (3′) positions shifts the HOMO level to higher energy, while replacing alkyl groups at the 9 (9′) positions by aryl groups shifts the HOMO level to lower energy. Furthermore, it has been found that the triplet energy of these compounds is determined by the presence of poly(*p*-phenyl) chains in the molecular structure. By identifying the longest poly(*p*-phenyl) chain, one can predict whether a compound will be a suitable host for a high-energy triplet emitter. An overview of HOMO levels, singlet and triplet levels, and exchange energies is given for all carbazole compounds synthesized. Finally, OLEDs employing two selected carbazole compounds as host and *fac*-tris(2-phenylpyridine)-iridium (Ir(ppy)₃) as guest were constructed and characterized electrically.

Introduction

A particularly appealing solution to achieve full-color organic light-emitting diodes (OLEDs) is energy or charge transfer from host molecules to emissive guest molecules. This process can be optimized to virtually 100% efficiency already at low guest concentrations. In particular, the use of phosphorescent emitters as guests, which give an increase in the efficiency of light-emitting diodes because they can harvest triplet excitons, has stimulated the development of metal-containing electroluminescent guest systems.[1,2] The host for such phosphorescent or triplet emitters has to fulfill—besides the customary requirements known already from the use of fluorescent emitters—the additional condition that the triplet energy of the host has to be higher than that of the guest.[3] This condition arises not only due to the preference for exothermic energy transfer processes from host to guest but also, and maybe even more importantly, due to the condition that transfer of triplet excitons from guest to host must be prohibited.

For OLEDs, a prominent class of materials that fulfills the above-mentioned boundary conditions is the class of carbazoles.

Many carbazole derivatives have a sufficiently high triplet energy to be able to host red,[2,4–6] green,[7,8] and in some cases even blue[9,10] triplet emitters. Carbazole derivatives can be used as host material for both small-molecule and polymer OLEDs. Often used in this respect for polymer OLEDs is a polymer that has initially been widely applied as photoconductor in photocopying machines: poly(9-vinylcarbazole) (PVK).[11–16] Essentially, PVK consists of a nonconjugated main chain with carbazole units attached as side groups. As such, PVK can be treated as a collection of carbazole molecules. For small-molecule OLEDs, a carbazole derivative that is often used as host for triplet emitters is 4,4′-bis(9-carbazolyl)-biphenyl (CBP),

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resulting in maximum internal quantum efficiencies of 60 to 80%.[2,4-9,17-19]

Since the exchange energy[20] of many small molecules is found to be in the range of 0.7 to 1 eV[21] a large triplet energy is usually found for compounds with a very large singlet energy. In stable systems, a large singlet energy generally means a high oxidation potential and, consequently, a high barrier for hole injection from anodes such as indium tin oxide. Additional hole injection and transporting layers have to be introduced thereby complicating the device architecture. Moreover, the triplet energy of CBP (2.56 eV) is too small to yield highly efficient devices with blue triplet emitters so that hosts with even higher triplet energies (≥2.75 eV) are desired.[10]

Next to the luminescent behavior, the charge transporting properties of a molecule define its applicability as host in an electroluminescent device. Many carbazole derivatives are known to predominantly transport positive charge carriers. For example, PVK is often described in the literature as being a unipolar hole transporter.[22] Consequently, in a polymer OLED electron transporting compounds have to be admixed to the PVK layer to increase the charge carrier balance and shift the emission zone away from the cathode,[13,14] or extra layers (hole blocking and electron transporting) have to be used.[11,12,16] CBP is reported to have a more bipolar transport character.[23] Nevertheless, also in small-molecule OLEDs employing carbazole derivatives extra layers are often introduced to confine the positive charge carriers in the emission zone.

Currently, much effort is directed toward finding alternative carbazole derivatives as host materials for small-molecule OLEDs that address the above-mentioned issues. These efforts have resulted for example in the use of 4,4′,4″-tris(9-carbazolyl)-triphenylamine (TCTA),[24] 4,4′-bis(9-carbazolyl)-2,2′-dimethyl-biphenyl (CDBP),[25] and 3,5-bis(9-carbazolyl)benzene (mCP)[10] as host materials.

Common to the molecular structure of all the carbazole derivatives mentioned thus far is the derivatization via the nitrogen of the carbazole unit. In this report, we introduce alternative carbazole derivatives for small-molecule OLEDs based on derivatization at the phenyl rings of the carbazole unit.[26-28] The carbazole is either connected to other carbazoles to form carbazole dimers and trimers or to fluorene and oxadiazole to form mixed compounds. We have investigated the influence of substitution of carbazoles at the phenyl rings and at the nitrogen on spectroscopical and electrochemical properties relevant for OLEDs. It will be shown that the position

of the coupling site connecting the monomers to form oligomers determines the triplet energy. Furthermore, the HOMO level can be engineered by substitution at the 3, 6, and 9 position of the carbazoles (see compound **1** in Figure 1 for the numbering of the ring system) while at the same time a high triplet energy is maintained. Finally, electroluminescent devices are constructed to test two carbazole derivatives in a host−guest system with a phosphorescent metal complex as guest.

Experimental Section

Synthesis. All reagents and solvents were used as received or purified using standard procedures. NMR spectra were recorded on a Varian Mercury Vx at frequencies of 400 and 100 MHz for ^{1}H and ^{13}C nuclei or Varian Gemini 2000 at frequencies of 300 and 75 MHz for ^{1}H and ^{13}C nuclei, respectively. Details on the synthesis are provided in the Supporting Information section.

OLEDs. OLEDs were prepared by vacuum evaporation at a base pressure of about $1-2 \times 10^{-6}$ mbar. The substrates were cleaned with a detergent and 2-propanol and subsequently subjected to a O_2-plasma treatment for 10 min. The device layout is shown in an inset of Figure 5. *N,N′*-di(naphthalen-1-yl)-*N,N′*-diphenyl-benzidine (α-NPD), *fac*-tris-(2-phenylpyridine)-iridium Ir(ppy)$_3$, 2,9-dimethyl-4,7-diphenyl-phenan-throline (BCP) and tris(8-hydroxyquinoline)aluminum (Alq$_3$) were obtained from Sensient/Syntec and used as received. Voltage−current−luminance (U−I−L) curves were measured in nitrogen atmosphere by a HP 3245A universal source, Keithley 2000 multimeter and a LMT 1006 luminance meter.

Phosphorescence Measurements. The phosphorescence spectra were obtained on highly diluted (about 1 mg/l) solutions in methyl-THF, which gives a clear glass at 77 K. The emission spectra at 77 K were recorded with an Edinburgh 900 spectrofluorometer. Nongated and gated spectra were recorded to discriminate the phosphorescence from fluorescence. The gate delay was 500 μs with a gate width of 9 ms. The highest energy peak in the phosphorescence spectrum was taken for the $S_0^{\nu=0} \leftarrow T_1^{\nu=0}$ transition.

Cyclic Voltammetry (CV). Cyclic voltammetry measurements were recorded in dichloromethane, with 1 M tetrabutylammonium hexafluo-rophosphate as supporting electrolyte. The working electrode was a platinum disk (0.2 cm^2), the counter electrode was a platinum plate (0.5 cm^2), and a saturated calomel electrode (SCE) was used as reference electrode, calibrated against a Fc/Fc$^+$ couple. As the oxidation potential of SCE relative to the vacuum level is known (4.74 V[29]), the measured oxidation potentials can be converted into ionization potentials. In this report, we use the ionization potential as a measure for the energy of the highest occupied molecular orbital (HOMO). Although care has to be taken to compare HOMO levels obtained in this way to those obtained by other techniques (such as UPS), the HOMO levels of the oligomers *among* each other allow for excellent comparison.

Results and Discussion

1. Carbazole Oligomers. A series of carbazole compounds was synthesized and characterized spectroscopically, electro-chemically, and electrically (as a layer in an OLED). Carbazole monomers are linked via the 3 (6, 3′, 6′, etc.) positions to form dimers and trimers and substituted with either aryl- or alkyl-groups at the 9 positions (see Figure 1).

REDOX Stability of Carbazole Oligomers. Cyclic volta-mmetry measurements showed one or more oxidation waves and no reduction wave in the range of −1.4 V to +1.8 V vs SCE with dichloromethane as solvent. The first oxidation wave of the carbazole oligomers is reversible as opposed to the

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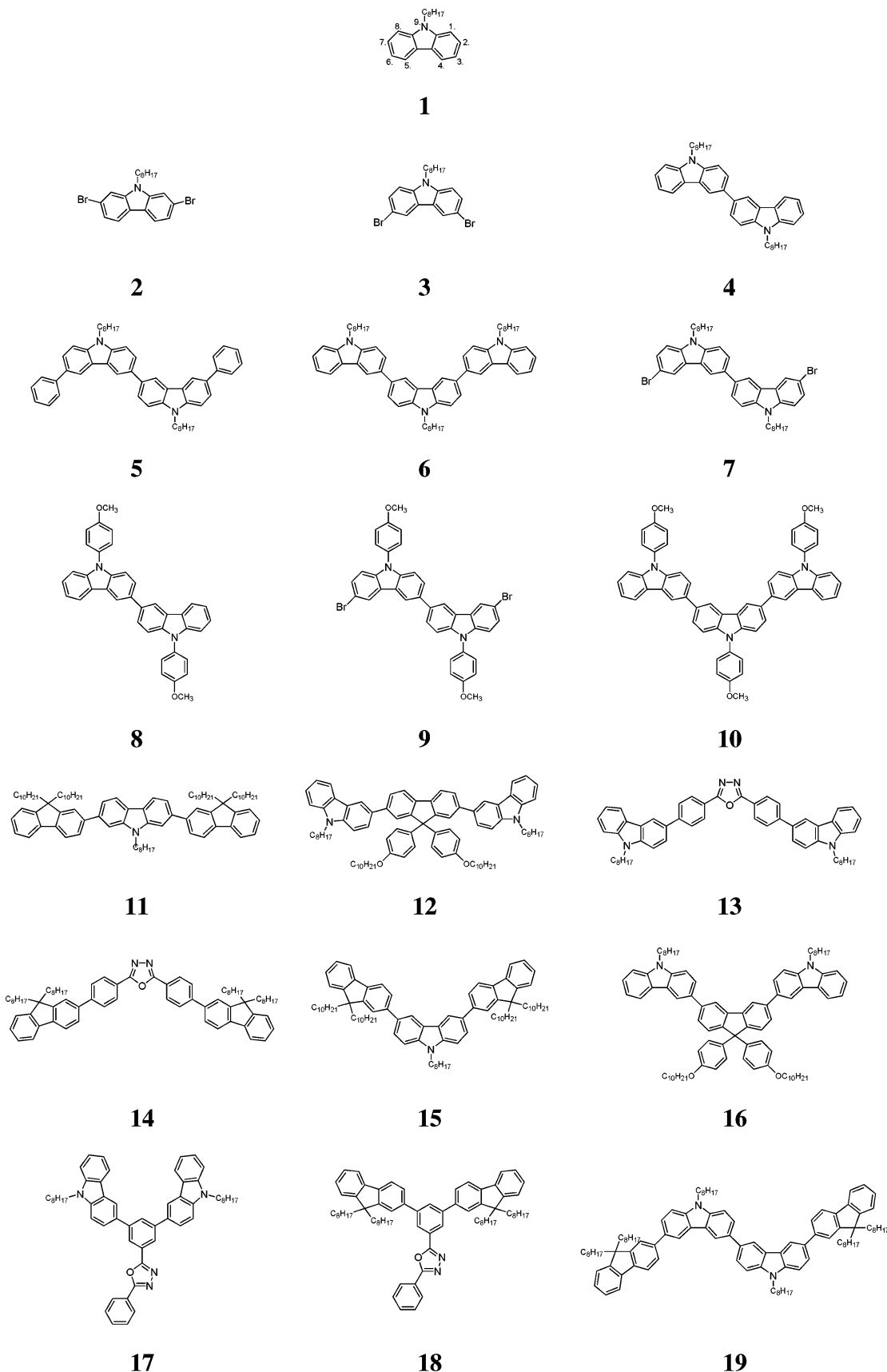
Figure 1. Chemical structures of the compounds studied in this report. At the top, the chemical structure and numbering of 9-octylcarbazole is shown (**1**).

oxidation waves of carbazole and its 9-substituted monomeric derivatives.[30] This important difference is due to the suppression of the N–N and C–C coupling reaction between carbazole

units, which are the chemical reactions that cause the irreversibility toward oxidation.[31] Carbazole monomers where the 3, 6, and 9 positions are substituted are electrochemically revers-

Table 1. Half-Wave Oxidation Potentials ($E_{1/2}^{ox}$, reversible unless otherwise indicated), Energies of the HOMO Level, Singlet Level (measured as $S_0^{v=0} \leftarrow S_1^{v=0}$ at 77 K), Triplet Level (measured as $S_0^{v=0} \leftarrow T_1^{v=0}$ at 77 K), and the Singlet−Triplet Energy Difference (ΔE_{ST}) for Compounds **1**−**19**

compd	$E_{1/2}^{ox}$ [V]	(HOMO) [eV]	$S_0^{v=0} \leftarrow S_1^{v=0}$ [eV]	$S_0^{v=0} \leftarrow T_1^{v=0}$ [eV]	ΔE_{ST} [eV]
1	1.14[b]	(−5.88)	3.50	3.02	0.48
2	1.35[b]	(−6.09)	3.49	2.88	0.61
3	1.45	(−6.19)	3.21[a]	2.93	0.28
4	0.86	(−5.60)	3.21	2.75	0.46
5	0.87	(−5.61)	3.16	2.74	0.42
6	0.83	(−5.57)	3.18	2.73	0.45
7	0.99	(−5.73)	3.12[a]	2.75	0.37
8	0.96	(−5.70)	3.25	2.75	0.50
9	1.05	(−5.79)	3.14[a]	2.76	0.38
10	0.89	(−5.63)	3.19	2.73	0.46
11	1.25[b]	(−5.99)	3.13	2.37	0.76
12	1.06	(−5.80)	3.12	2.38	0.74
13	1.20[b]	(−5.94)	3.02	2.44	0.58
14	1.70[b]	(−6.44)	3.14	2.34	0.80
15	1.04	(−5.78)	3.26	2.49	0.77
16	1.20[b]	(−5.94)	3.35	2.73	0.62
17	1.20[b]	(−5.94)	3.24	2.70	0.54
18	1.70[b]	(−6.44)	3.40	2.52	0.88
19	0.91	(−5.65)	3.18	2.48	0.70

[a] Measured at room temperature. [b] Irreversible oxidations (Peak potential is given).

ible.[31] Obviously, protection of the 3 and 6 positions through substitution or dimerization prevents C−C coupling at these positions. For example, 3,6-dibromo-9-octyl-carbazole (**3**) shows a reversible oxidation wave. Also, 9-substituted carbazole dimers are known to be extremely stable and to undergo reversible one-electron redox steps.[31] In this report, several carbazole dimers and trimers coupled at the 3 (3′) positions and substituted at the 9 positions, and several mixed compounds are found to be electrochemically stable. This is an important factor in the application of carbazole compounds in OLEDs especially if the compounds should be (at least partially) responsible for the transport of positive charge carriers in the diodes.

HOMO Level of Carbazole Oligomers. Two main substitution effects influence the position of the HOMO level in the carbazole compounds investigated in this report. The first effect is related to substitutions at the 2/7 and 3/6 positions. For bromine as substituent, cyclic voltammetry measurements indicate that the HOMO is shifted to lower energy. Furthermore, substitution of bromine at the 2 and 7 positions of 9-octylcarbazole (**2**) influences the position of the HOMO level less than substitution at the 3 and 6 positions (**3**). Similarly, the HOMO level of **7** is shifted to lower energy with respect to the HOMO level of **4** (see Table 1).

Generally, when attaching electron withdrawing substituents (such as bromine) to conjugated molecules, the electron density in the π-system of the conjugated molecule is decreased. Consequently, the molecule is stabilized and the oxidation potential is increased, corresponding to a shift of the HOMO level to lower energy. Apparently, for carbazole such a stabilizing effect is stronger for substitution at the 3 and 6 positions than for substitution at the 2 and 7 positions. This can be explained by the fact that for the HOMO of the carbazole molecule, the electronic density at the 2 and 7 positions is less than at the 3

and 6 positions.[30] Therefore, substituting the 2 and 7 positions with electron withdrawing groups will have less influence on the electron density of the carbazole molecule than substituting the 3 and 6 positions. As can be deduced from the considerable increase in oxidation potential, effective HOMO level tuning by bromine substitution of carbazole is mainly achieved by inductive electron withdrawing effects. The weak mesomeric electron donating effect of bromine, that destabilizes carbazole and can stabilize a carbocation, which should consequently result in a lower oxidation potential than the unsubstituted compound, is apparently negligible compared to the inductive effect.

Upon going from the monomer **1** to the dimer **4** a large shift of the HOMO level to higher energy is observed. The HOMO level shifts to even higher energy upon going from the dimer **4** to the trimer **6**, albeit only slightly (the shift is close to the limit of experimental accuracy, but the trend is clear). Attaching phenyl groups to the 3 and 6′ positions of **4** to form **5**, has no influence on the position of the HOMO level.

The second substitution effect is related to the 9 position. CBP, which was mentioned in the Introduction as being a prominent host material for small-molecule OLEDs, is a carbazole dimer in which the carbazoles are connected via their nitrogen atoms with a biphenyl bridge. Contrary to dimerization via the 3 (3′) position, dimerization via the 9 (9′) position leads to a shift of the HOMO level to lower energy. For carbazole oligomers, a similar effect is observed when replacing alkyl groups at the 9 positions (**4**, **6**, and **7**) by aryl groups (**8**, **9**, and **10**). Apparently, an alkyl group on the 9 position activates the carbazole ring system by increasing the electron density and makes the compound easier to oxidize than the corresponding aryl-substituted compound. As the aryl group is twisted with respect to the carbazole ring system, it is not involved in delocalization of π-electrons in the carbazole ring system.

The effects, substitution at the 9 position and at the 3 and 6 positions, are additive. The substitution effects can act cumulative on the position of the HOMO level, which is clear from comparing compounds **4**, **8**, and **9** where the HOMO level progressively shifts to lower energy from −5.60 eV to −5.79 eV. The substitution effects can also act against each other, which is clear from comparing compounds **4**, **6**, and **10** (again, it is rather the trend over a series of measurements than the absolute differences which is important here). In this series, the HOMO level is first shifted to higher energy upon attaching a third carbazole. The HOMO level is shifted back again by replacing the alkyl groups at the 9 positions by aryl groups.

The above shows that a method has been found to tune the HOMO level of carbazole compounds by substitution at the 3, 6, and/or 9 positions. Connecting carbazole molecules via their 3 (3′) positions shifts the HOMO level to higher energy while replacing alkyl groups at the 9 position by aryl groups shifts the HOMO level to lower energy. A toolbox for HOMO level engineering of carbazole compounds is now available that can be used to match the HOMO levels to the levels of hole injection and/or transport layers, thereby facilitating the injection of positive charge carriers.

Singlet and Triplet Energy of Carbazole Oligomers. The importance of the position of the energy levels depends not only on the neighboring charge injection and/or transport layers but also on the composition of the light-emitting layer itself. In

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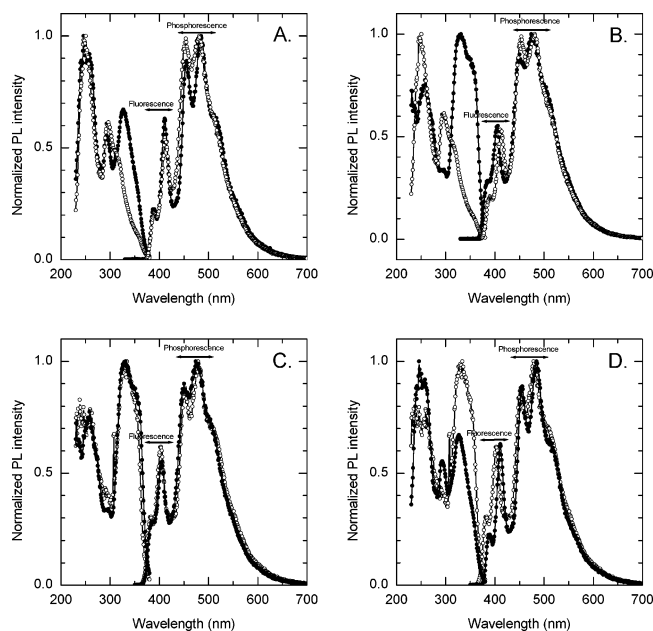
Figure 2. Photoluminescence excitation (measured at room temperature) and emission (measured at 77 K, nongated) spectra. A: **10** (solid circles) and **6** (open circles), B: **4** (solid circles) and **6** (open circles), C: **4** (solid circles) and **8** (open circles), D: **10** (solid circles) and **8** (open circles). The excitation wavelength is 330 nm and the emission wavelength is 400 nm for the emission and excitation spectra, respectively.

highly efficient small-molecule OLEDs the emissive layer consists of a phosphorescent guest dispersed in a host material.[1] Apart from the importance of matching the HOMO and LUMO level of the host material with the Fermi levels of the electrodes or the HOMO/LUMO levels of neighboring layers, the host material should have a higher triplet energy than the phosphorescent guest to prevent triplet energy transfer from the guest to the host. Although endothermic energy transfer has been reported in the literature,[9] exothermic energy transfer is favored for its higher efficiency.[10] So, a necessary boundary condition for the applicability of carbazole compounds as host in host−guest systems is that upon chemical modification the triplet energy of the host does not decrease below a certain limit set by the triplet energy of the phosphorescent guest.

All nonbrominated compounds show both singlet and triplet emission at low temperature (see Figure 2 for spectra of **4**, **6**, **8**, **10**).

For the singlet and triplet emissions of all compounds, the spectral envelopes and the energetical spacing of the vibronic progressions are the same. This indicates that the main contributions to singlet and triplet emission result from the same molecular species and decay to the same ground state. The ratio of singlet to triplet emission as taken from nongated spectra is approximately the same for all investigated carbazole compounds (Figure 2). The energies are summarized in Table 1. The bromine-substituted compounds **2**, **3**, **7**, and **9** behave differently. At low temperature, no singlet emission at all could be observed for **3**, **7**, and **9**, and only very little for **2**. This is due to the heavy atom effect brought about by the bromines, which causes the intersystem crossing yield to be close to 100%.[32]

For the carbazole compounds investigated in this report, the presence of bromine atoms has a small effect on the energy of

the triplet emission. For the monomer, the triplet emission is shifted only by about 0.09 eV to lower energy upon attaching bromines at the 3 and 6 positions (compare **1** and **3**), while a similar substitution pattern has no effect on the triplet energy of the dimers (compare **4**, **7** and **8**, **9** in Table 1).

However, dimerization has a strong effect on the triplet energy. For example, the energy of the triplet emission decreases by 0.27 eV when going from the monomer **1** to the dimer **4**. From a dimer to a higher oligomer, the triplet energy is hardly influenced, as is clear from comparing the dimer **4** to the trimer **6**. Replacing alkyl groups at the 9 positions with aryl groups does not influence the triplet energy significantly (for example, compare **4** and **8** in Table 1).

A high triplet energy is not the only prerequisite for a material that is to be used as host for a triplet emitter in an OLED. High triplet energies can usually be obtained by using materials with high singlet energies. However, in addition to the requirement of a high triplet energy, a good host material is required to have favorable HOMO and LUMO levels for charge injection from neighboring layers. In other words, for a good host material the exchange energy should be as small as possible to allow for both efficient charge injection into the host and efficient triplet emission from a dispersed triplet emitter.[33]

For the monomers the magnitude and direction of the exchange energy shift ΔE_{ST} depends on the substitution pattern: substitution at the 2 and 7 positions does not influence the singlet energy (compare **1** and **2**), whereas substituting at the 3 and 6 positions leads to a large decrease of the singlet energy (compare **1** and **3**, where the singlet energy decreases by 0.29 eV). On the other hand, the triplet energy depends much less on the substitution pattern. For example, the triplet energy decreases by 0.09 eV for substitution at the 3 and 6 positions (compare **1** and **3**) and by 0.14 eV for substitution at the 2 and 7 positions (compare **1** and **2**). For the monomer, bromine substitution at the 3 and 6 positions results in a decrease of ΔE_{ST} by 0.20 eV (compare **1** and **3**). Substitution of bromine at the 2 and 7 positions of the monomer results in an increase of ΔE_{ST} by 0.13 eV (compare **1** and **2**).
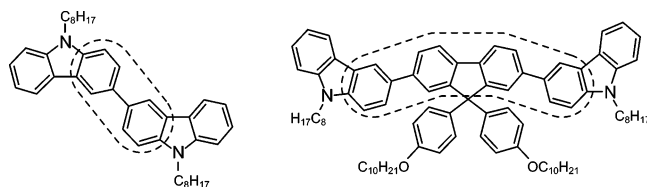
Dimerization influences both the singlet energy and the triplet energy. From monomer to dimer, the singlet and triplet energies both shift to lower values (compare **3** and **7**, and/or **1** and **4** in Table 1). Bromine substitution at the 3 and 6′ position of the dimer results in a decrease of ΔE_{ST} by 0.09 eV (compare **4** and **7**).

From dimer to trimer, the singlet and triplet energies are hardly influenced (compare **4** and **6**, and/or **8** and **10** in Table 1).

These shifts in singlet and triplet energy give rise to several interesting conclusions. First, in carbazole oligomers coupled via the 3 (3′) positions, the delocalization of the triplet wave function does not extend significantly beyond two carbazole units but is also not limited to one carbazole unit (see below, Table 1 and Figure 3).

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(33) The exchange energy is difficult to measure directly since the $S_0^{v=0} \rightarrow T_1^{v=0}$ absorption transition is not easily accessible. Although relaxation effects in these molecules are small (the Stokes shift is small and only slightly temperature dependent) it is not entirely appropriate to take the difference between the singlet absorption (i.e., not accounting for relaxation effects) and the triplet emission (i.e., accounting for relaxation effects) as measure for the exchange energy. Therefore, the energy difference (ΔE_{ST}) between the singlet and triplet emission transitions at 77 K is taken as estimate for the exchange energy.

Figure 3. Chemical structures of compounds **4** (left) and **12** (right). The longest poly(*p*-phenyl) chain is enclosed in a dashed line. For compound **4**, the longest poly(*p*-phenyl) chain is biphenyl, while for compound **12** this is quater(*p*-phenyl).

For the monomer, the triplet energy changes upon dimerization or bromine substitution. For the dimer, the triplet energy remains fairly constant if an additional carbazole is attached or if the dimer is substituted at the 3 and 6′ positions. Second, the singlet excited state differs significantly at the 3/6 and 2/7 positions. As can be deduced from the influence of bromine substitution on the singlet energy, the singlet excited state has less electron density at the 2 and 7 positions than at the 3 and 6 positions. This is known from theory on ring activation in organic synthesis.[34] For the triplet excited state, the 2/7 and 3/6 positions are more equivalent. Furthermore, it appears that the singlet and triplet energies are influenced by both inductive and mesomeric effects since attaching electron withdrawing bromines shifts the emission to lower energy, as does coupling an additional carbazole unit. In the latter case the shift is probably due to an increase in π-electron delocalization. Coupling an additional carbazole to the dimer has more influence on the singlet energy than on the triplet energy (compare **8** and **10**, and/or **4** and **6** in Table 1). Apparently, a singlet exciton is more delocalized than a triplet exciton, which promises an even further decrease of ΔE_{ST} when going to carbazole polymers.

Regarding the triplet energies of the compounds studied in this report, more insight can be gained by looking at polyphenyl molecules. The triplet energy of polyphenyl molecules decreases as the number of phenyl groups increases. From benzene to biphenyl to *p*-terphenyl, the triplet energy decreases from 3.65 to 2.84 eV to 2.55 eV, respectively. However, from biphenyl to *m*-terphenyl, the triplet energy hardly changes (2.84 eV for biphenyl, and 2.81 eV for *m*-terphenyl).[32] This is in accordance with studies on polyphenyl molecules that have shown that for poly(*p*-phenyl) molecules the conjugated system is delocalized along the longest molecular axis, and that for *m*-polyphenyl molecules the triplet state is localized at every composing biphenyl structure.[35,36] In this respect, it is interesting to note that the triplet energies of fluorene and carbazole (2.95 and 3.05 eV respectively) are higher than that of biphenyl. However, for [3,3′]-bicarbazolyl the triplet energy has decreased to a value close to that of biphenyl (see **4** in Tabel 1). This indicates not only that in [3,3′]-bicarbazolyl the triplet exciton is more delocalized than in carbazole, but also that the triplet exciton is predominantly delocalized over the biphenyl structure that is shared between the two carbazole units (see Figure 3). This explains why the triplet energy changes from a monomer to a dimer, but remains constant from a dimer to a trimer. As a first-order approximation, one could say that the triplet energy of

the carbazole compounds studied here is determined by the longest poly(*p*-phenyl) chain that can be identified in the molecular structure. To maintain a high triplet energy, the longest poly(*p*-phenyl) chain in the molecular structure should be as short as possible. For compounds **4** to **10**, the longest poly(*p*-phenyl) chain is a biphenyl structure, and for all these compounds the triplet energy is similar (2.73−2.76 eV) and close to that of biphenyl (2.84 eV). While the triplet energy is similar for compounds **4** to **10**, the position of the HOMO levels can be quite different, depending on the substitution pattern. This shows that the carbazole oligomers described here are a class of materials for which the HOMO levels can be adjusted within a certain range without influencing the triplet energy, giving great freedom in molecular engineering of suitable hosts for efficient OLEDs.

2. Mixed Carbazole/Oxadiazole/Fluorene Compounds. A second series consists of mixed compounds (**11** to **19** in Figure 1). These compounds contain two different units: a central unit and two identical end units. The central unit is either a carbazole derivative (9-octylcarbazole in **11** and **15**, and 9,9′-dioctyl-[3,3′]-bicarbazolyl in **19**), a fluorene derivative (9,9-bis[4-(3,7-dimethyloctyloxy)phenyl]fluorene in **12** and **16**) or an oxadiazole derivative (2,5-diphenyl-[1,3,4]-oxadiazole in **13**, **14**, **17**, and **18**). The end units are either a fluorene derivative (9,9-bis(3,7-dimethyloctyl)fluorene in **11**, **14**, **15**, **18**, and **19**) or a carbazole derivative (9-octylcarbazole in **12**, **13**, **16**, and **17**). This series of mixed compounds enables us to study the influence of the coupling of π-conjugated aromatic and hetero-aromatic systems on the singlet and triplet energies. Furthermore, as carbazole derivatives are known to mainly transport holes, attaching electron transport moieties (such as oxadiazole derivatives) might be necessary to achieve balanced charge transport in OLEDs. Ultimately, this should lead to a design rule that results in compounds with high triplet energies and suitable HOMO and LUMO levels for charge injection by commonly used injection layers.

REDOX Stability and HOMO Levels of Mixed Compounds. The mixed compounds **11** to **18** behave differently upon oxidation. The compounds **11** and **12** and all oxadiazole-containing compounds show irreversible oxidation waves. For the compounds with oxadiazole as the central unit, the way in which the end groups (carbazole or fluorene) are connected to the central unit does not influence the position of the HOMO level at all (compare **13** and **17**, and/or **14** and **18**). For the compounds with fluorene (**12** and **16**) and carbazole (**11** and **15**) as the central unit, a lower oxidation potential is observed when the end groups are coupled to the 3 and 6 positions (**15** and **16**) than when they are coupled to the 2 and 7 positions (**11** and **12**). However, the most striking feature is the change from irreversible to reversible oxidation behavior in the pairs **11**−**15** and **12**−**16**. Coupling the end groups to the 3 and 6 positions not only shifts the oxidation potential to lower levels but also ensures stable redox behavior analogous to what was found for the carbazole compounds **3**−**10**.

Singlet and Triplet Energy of Mixed Compounds. The triplet emission spectra of the mixed compounds resemble the singlet emission spectra in most cases (the exception is compound **17** which shows excimer emission) except that the triplet emission spectra show more vibrational structure. This spectral resemblance is a good indication that both the singlet

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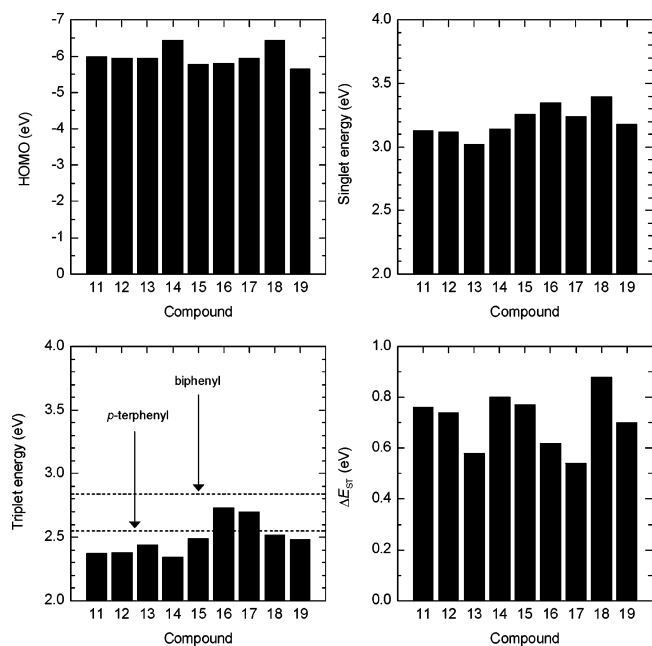
Figure 4. Energies of the HOMO level, singlet emission, and triplet emission, and the exchange energy (ΔE_{ST}) for the mixed compounds **11** to **19**. In the bottom left graph the triplet emission energies of biphenyl and *p*-terphenyl are indicated by dashed lines.

and the triplet state decays to the same ground state. The triplet emission energies of the mixed compounds are shown graphically in Figure 4.

For comparison purposes, the triplet energies of biphenyl and *p*-terphenyl are also shown. By comparing the triplet energies of the mixed compounds to those of biphenyl and *p*-terphenyl, one can recognize three different subgroups: (a) compounds with a triplet energy significantly lower than that of *p*-terphenyl (**11** to **14**), (b) compounds with a triplet energy similar to that of *p*-terphenyl (**15**, **18**, and **19**), and (c) compounds with a triplet energy close to that of biphenyl (**16** and **17**). In the compounds from subgroup (a) one can recognize long poly(*p*-phenyl) chains (for example, in compound **12** one can recognize a quater (*p*-phenyl) structure, see Figure 3). It is also clear that the delocalization of the triplet exciton extends across the oxadiazole central unit, as can be deduced from the low triplet energy of compounds **13** and **14**. In the compounds from subgroup (b), one can recognize *p*-terphenyl structures as the longest poly-(*p*-phenyl) chains. Consequently, the triplet energies of these compounds (**15**, **18**, and **19**) are similar to that of *p*-terphenyl. The longest poly(*p*-phenyl) chain that can be recognized in the compounds from subgroup (c) is a biphenyl structure. Therefore, the triplet energies of these compounds (**16** and **17**) are close to that of biphenyl.

The compounds investigated here differ in the degree of delocalization of the triplet exciton. The higher the degree of delocalization, the lower the triplet energy. By identifying the longest poly(*p*-phenyl) chain (such as biphenyl or *p*-terphenyl), one can predict whether a compound will be a suitable host for a high-energy triplet emitter. In this respect, one wants to limit the longest poly(*p*-phenyl) chain to biphenyl, as the presence of the next higher poly(*p*-phenyl) chain (*p*-terphenyl) decreases the triplet energy too much.

3. OLEDs with Carbazole Compounds as Host for a Triplet Emitter. In the previous paragraphs a number of
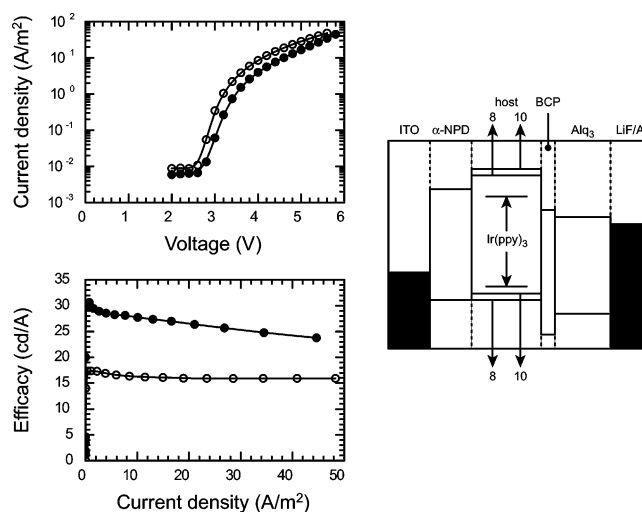
Figure 5. Current density as a function of applied voltage (top left) and efficacy as a function of current density (bottom left) for devices employing compound **8** (solid circles) and compound **10** (open circles) as host for the triplet emitter Ir(ppy)$_3$. The device layout is shown on the right. Here, α-NPD stands for *N,N′*-di(naphthalen-1-yl)-*N,N′*-diphenylbenzidine (HOMO −5.7 eV, LUMO −2.6 eV), Ir(ppy)$_3$ for *fac*-tris(2-phenylpyridine)-iridium (HOMO −5.5 eV, LUMO about −3 eV), BCP stands for 2,9-dimethyl-4,7-diphenyl-phenanthroline (HOMO −6.7 eV, LUMO −3.2 eV), and Alq$_3$ stands for tris(8-hydroxyquinoline)aluminum (HOMO −6.0 eV, LUMO −3.3 eV).

potential host materials for OLEDs and some of their properties were introduced. All of the materials were specifically designed to be used as hosts for triplet emitters. It is beyond the scope of this paper to present an exhaustive electrical characterization of devices employing these materials. In this paper, we concentrate on the importance of matching the properties of the host to the boundary conditions introduced by using a triplet emitter as guest. For example, the situation could occur that optimizing the HOMO level of the host for good charge injection shifts the HOMO of the host above the HOMO of the guest thereby decreasing the efficiency of charge recombination on the guest.

To be used as host material in an OLED, the dimer **8** and the trimer **10** were selected. These compounds have different HOMO level energies but similar triplet energies (see Table 1). Based on the latter property, both compounds should be equally suited to accommodate the green light-emitting metal complex *fac*-tris(2-phenylpyridine)-iridium (Ir(ppy)$_3$), whose emission is around 2.42 eV. Due to their large triplet energy both compounds are in principle also suitable as host for blue light-emitting triplet emitters. Furthermore, both compounds show excellent film forming qualities, are stable toward oxidation, have the same phosphorescence quantum yield, and can be evaporated without decomposition.

OLEDs with **8** and **10** as host and 8% (mass ratio) of Ir(ppy)$_3$ as guest were constructed and their electrical characteristics were measured (see Figure 5). Note that a hole injecting/transporting layer of *N,N*-di(naphthalen-1-yl)-*N,N′*-diphenyl-benzidine (α-NPD) was used to minimize effects due to differences in charge injection into **8** and **10** at the anode. As α-NPD has a relatively low-lying HOMO level at −5.7 eV, using this material will result in the absence of an energy barrier for hole injection for both host materials.

The electroluminescence of all devices consists only of green emission from Ir(ppy)$_3$ without any residual emission from the

host and/or adjacent layers. From Figure 5 it is apparent that subtle changes in HOMO level energy have a major impact on both current density and efficacy. The current density increases by a factor of 5 at voltages between ca. 2.5 and 4.5 V to 3 at higher voltages when the HOMO level is shifted from −5.70 eV (**8**) to −5.63 eV (**10**). This is even more remarkable if one realizes that for both hosts no hole injection barrier exists at the α-NPD interface. Also, the efficacy decreases upon replacing **8** by **10** as host material.

The higher current density for the host with the lower oxidation potential is most likely due to an increase in positive charge density. The higher positive charge carrier density results in a charge carrier imbalance and quenching of the excited states. Both effects will result in a decrease in efficacy. There are two possible sources for the increase in positive charge carrier density. The first one is related to the injection contact. Despite the use of α-NPD as a hole injection layer with low-lying HOMO level, more charge can be injected into the host with the lower oxidation potential. The second one is related to the interplay of the HOMO level of the host with that of the triplet emitter. Different to standard hosts for Ir(ppy)$_3$, such as CPB or PVK which have a HOMO level below −5.7 eV, the HOMO levels of the carbazole compounds studied in this report are at energies closer to the HOMO level of Ir(ppy)$_3$. Ir(ppy)$_3$ has a reversible oxidation at 0.72 V vs SCE (literature values give a range from 0.70 to 0.77 V vs SCE[37−40]), which corresponds to a HOMO level at about −5.46 eV. The differences in current density and efficacy for **8** and **10** are a consequence of the higher oxidation potential of **8** in combination with sequential charge carrier trapping on Ir(ppy)$_3$ as the main source for the formation of the excited state. As the HOMO of Ir(ppy)$_3$ is positioned only slightly above the HOMO of **10**, Ir(ppy)$_3$ acts as a shallow trap for positive charge carriers. The positive charge carriers will therefore not only reside on the guest emitter but also on the host thereby preventing efficient charge recombination on the guest. When dispersed in compound **8**, Ir(ppy)$_3$ acts as a deep trap for both types of charge carriers. Consequently, the efficiency of recombination via sequential trapping is increased, and the current density is decreased.

An excited state of the triplet emitter can also be formed via excited state energy transfer from the host. This is unlikely to occur as the LUMO of the host is situated above the LUMO of Ir(ppy)$_3$.[8] (the position of the LUMO of the host is determined by adding the optical band gap energy to the HOMO level).

This means that in all compounds, Ir(ppy)$_3$ will act as a trap for electrons rendering excited state formation on the host highly unlikely.

Whichever of the mechanisms described above dominates and causes the differences in charge density and efficacy for the two hosts with different oxidation potentials, the device measurements unambiguously demonstrate that it is indeed possible to match hosts for high energy triplet emitters with hole injection contacts in the range of around −5.6 eV and achieve efficient emission from a dispersed triplet emitter.

Conclusion

The electrical and optical properties of carbazole compounds strongly depend on the substituents and the substitution pattern. The HOMO level of carbazole compounds can be tuned by substitution at the 3, 6, and/or 9 positions while the triplet level remains sufficiently high to accommodate even blue triplet emitters. After an initial shift upon dimerization of the carbazoles the triplet energy stays constant at about 2.75 eV due to the localization of the triplet exciton over the biphenyl structure that is shared between two carbazole units.

By using mixed carbazole/oxadiazole/fluorene compounds we have established a relation between the coupling of the π-conjugated aromatic system and the triplet (and singlet) energies. The triplet energy is determined by the presence of poly(*p*-phenyl) chains in the molecular structure. By identifying the longest poly(*p*-phenyl) chain one can predict whether a compound can be used as a suitable host for a certain triplet emitter.

These design rules can be exploited to make hosts for OLEDs that not only have high triplet energies but also favorable energy levels for charge injection from neighboring layers. In a next step we attempt to use the carbazole compounds presented in this report as building blocks for polymers that are to be used as hosts for triplet emitters in OLEDs. We expect that the same structural elements that determine the triplet energies of small molecules will play a similarly important role for the triplet energies of polymers. An interesting question in this context is to what extent does polymerization influence the singlet and triplet energies, since they determine the exchange energy of the polymer.

Supporting Information Available: Synthesis, ^{1}H NMR, ^{13}C NMR spectra, melting points, elemental analysis and electrochemical data of compounds **1** − **19** (pdf). This materials is available free of charge via the Internet at http://pubs.acs.org.

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