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Well Defined Carbazol-3,9-Diyl Based Oligomers as Host Materials for Organic Electro-Phosphorescent Devices

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Well Defined Carbazol-3,9-Diyl Based Oligomers as Host Materials for Organic Electro-Phosphorescent Devices

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Well defined carbazol-3,9-diyl-based derivatives as host materials for electrophosphorescent devices have been synthesized by the modified Ullmann reaction as a key step. The full characterization of their structure by mass spectrometry, infrared absorption and proton magnetic resonance spectroscopy is presented. The amorphous compounds with glass transition temperatures of $103-154^{\circ}C$ possess high thermal stability with onset decomposition temperatures exceeding $360^{\circ}C$. Conjugation of the 3,9-linked systems is rather confined within one carbazole unit, retaining large triplet energies suitable for green and red electrophosphorescence. Using the new host material, efficient green phosphorescent organic light emitting diodes was demonstrated.

Keywords: amorphous material; aromatic amine; electrophosphorescence; light emitting diode

INTRODUCTION

Improvements in organic light emitting diodes (OLEDs) performance over the past decade have resulted in commercially available products.

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Organometallic small molecule phosphor-doped devices have demonstrated by far the highest efficiency with >90% internal quantum efficiency [1,2]. In phosphorescent OLEDs, to reduce quenching associated with relatively long excited-state lifetimes of triplet emitters and triplet-triplet annihilation etc., triplet emitters of heavy-metal complexes are normally used as emitting guests in a host material, and thus effective host materials are of equal importance for efficient phosphorescent OLEDs. For electrophosphorescence from triplet guests, it is essential that the triplet level of the host be larger than that of the triplet emitter to prevent reverse energy transfer from the guest back to the host and to effectively confine triplet excitons on guest molecules [3,4].

Here, we report a molecular design for large-gap materials adopting the non-conjugated linking of carbazolyl moieties. The 3,9'-linked carbazoles demonstrate large triplet energies and serve as effective host materials for green electro-phosphorescent devices.

2. EXPERIMENTAL

2.1. Instrumentation

Fourier transform infrared (FTIR) spectra were measured using a Bio-Rad Digilab FTS-40 spectrometer. ¹H NMR spectra were recorded using a Bruker DPX 250 apparatus. Mass spectra were obtained on a Varian MAT-312-Spectrometer Waters ZQ 200 spectrochromatograph.

Ultraviolet (UV) spectra were measured with a Shimadzu UV-1601PC spectrophotometer. Photoluminescence (PL) spectra were measured using a charge-coupled-device (CCD) spectragraph and the 325-nm line of the He-Cd laser as the excitation source. Phosphorescence spectra of compounds were measured at 77 K with an IBH picosecond photon detection module and a sub-microsecond Xenon flash lamp as an excitation source using a 5 ms delay time between the excitation with a microsecond flash lamp and the measurement.

Differential scanning calorimetry (DSC) measurements were carried out using a TA Instrument DSC-2920 calorimeter. Thermogravimetric analysis (TGA) was performed on a TA Instrument 2950 TGA thermal analyzer. The measurements were recorded in a nitrogen atmosphere at a heating rate of 10° C/min.

OLEDs were fabricated on the ITO-coated glass substrates with multiple organic layers sandwiched between the transparent bottom indium-tin-oxide (ITO) anode and the top metal cathode. The PEDT:PSS layer was prepared by spin coating, and other material layers were deposited by vacuum evaporation in a vacuum chamber with a base pressure of $<10^{-6}$ torr. The deposition rate of organic layers was kept at $\sim 0.2 \text{ nm/s}$. The active area of the device is 1 mm^2 , as defined by the shadow mask for cathode deposition. The current-voltage-brightness characterization of the light-emitting devices was performed with a source-measurement unit and a Si photodiode calibrated with Photo Research PR650. Electroluminescence (EL) spectra of the devices were collected by a calibrated CCD spectragraph.

2.2. Materials

Polyethylene dioxythiophene/polystyrene sulphonate (PEDOT/PSS) was received from Bayer Corp. 1,4-Bis(1-naphthylphenylamino)biphenyl (NPD), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), tris(2-phenylpyridine)-iridium (Ir(ppy)₃) and tris-(8-hydroxyquinoline) aluminium (Alq₃) were received from SynTec Gmbh. The materials were used in this study for preparation of multilayer electroluminescent devices.

9H-Carbazole (1), *t*-butylchloride, diphenylamine, copper powder, 4iodoanizole and 18-crown-6 were purchased from Aldrich and used as received. 3,6-Di(*t*-butyl)-9H-carbazole (2) was synthesized from 9H-carbazole (1) and *t*-butylchloride using Friedel- Crafts alkylation [5]. 3-Iodo-9H-carbazole (3) was obtained by a procedure of Tucker [6]. 3-Iodo-9-ethylcarbazole (4) was prepared by alkylation of 3-iodo-9H-carbazole (3) with ethyliodide in the presence of a phase transfer catalyst [7]. Diphenylamino end-capped di(carbazol-3,9-diyl) with secondary amine functions (5) was prepared by similar procedure as we described earlier [8].

3-[3,6-Di(*t*-butyl)carbazol-9-yl]-9-ethylcarbazole (**6**) 2 g (6.2 mmol) of 3-iodo-9-ethylcarbazole (**4**), 1 g (3.6 mmol) of 3,6-di(*t*-butyl)carbazole (**2**), powdered potassium carbonate (1.9 g, 14.4 mmol), copper powder (0.46 g, 7.2 mmol) and 18-crown-6 (0.17 g, 0.64 mmol) were refluxed in o-dichlorobenzene (10 ml) under nitrogen for 24 h. Copper powder and inorganic salts were then removed by filtration of the hot reaction mixture. The solvent was distilled under reduced pressure and the crude product was purified by silica gel column chromatography using hexane/ethylacetate (vol. ratio 20:1) as an eluent. Yield of the compound **6** was 71%. IR (KBr), ν/cm^{-1} : 3054, 2973 (C–H, Ar), 1588, 1492 (CH=CH, Ar), 1274 (C–N), 1230, 1067, 746 (CH=CH, Ar). ¹H NMR (CDCl₃), δ (ppm): 1.41–1.63 (m, 21H, -C(CH₃)₃ and -CH₃), 4.42 (q, 4H, J–7.2 Hz, =NCH₂–), 7.16–8.45 (m, 13H, Ar). MS, m/z (%): 473 (100), 459 (47), 346 (22).

Ethyl-substituted ter(carbazol-3,9-diyl) with diphenylamino endcap (7) was prepared by the following procedure. 2.5 g (~5 mmol) of the derivative having secondary amine function (5), 3.33 g (10.35 mmol) of 3-iodo-9-ethylcarbazole (4), copper powder (1.13 g, 17.83 mmol), 18-crown-6 (0.23 g, 0.89 mmol) and potassium carbonate (4.24 g, 30.76 mmol) were dissolved in o-dichlorobenzene. The solution was stirred at 180°C for 24 h. Copper powder and inorganic components were then removed by filtration of the hot reaction mixture. The crude product was precipitated into 250 ml of methyl alcohol and purified by silica gel column chromatography using hexane/ ethylacetate (vol. ratio 45:1) as an eluent. Yield of the compound 7 was 30%. IR (KBr), ν/cm^{-1} : 3053, 2974 (C–H, Ar), 1588, 1493 (CH=CH, Ar), 1274 (C–N), 1229, 1067, 747 (CH=CH, Ar). ¹H NMR $(CDCl_3), \delta$ (ppm): 1.49 (t, 6H, J=7.25 Hz, $-CH_3), 4.39$ (q, 4H, J=7.2 Hz, -NCH₂-), 6.86-8.55 (m, 31H, Ar). MS, m/z (%): 694 (26), 693 (47), 502 (100), 361 (22).

Methoxyphenyl-substituted di(carbazol-3,9-diyl) with diphenylamino end-cap (**8**) was prepared by the following procedure. 2.5 g (~5 mmol) of the derivative having secondary amine function (**5**), 2.25 g (9.9 mmol) of 4-iodoanizole, copper powder (1.13 g, 17.83 mmol), 18-crown-6 (0.23 g, 0.89 mmol) and potassium carbonate (4.24 g, 30.76 mmol) were dissolved in o-dichlorobenzene. The solution was stirred at 180°C for 24 h. Copper powder and inorganic components were then removed by filtration of the hot reaction mixture. The crude product was precipitated into 200 ml of methyl alcohol and purified by silica gel column chromatography using hexane/ethylacetate (vol. ratio 50:1) as an eluent. Yield of the compound **8** was 34%. IR (KBr), ν/cm^{-1} : 3073, 2969 (C–H, Ar), 2834 (OCH₃), 1588, 1493 (CH=CH, Ar), 1274 (C–N), 1229, 1067, 998, 789 747 (CH=CH, Ar). ¹H NMR (CDCl₃), δ (ppm): 3.87 (s, 3H, –OCH₃), 6.72–8.95 (m, 28H, Ar). MS, m/z (%): 606 (100), 504 (74), 421 (82).

3. RESULTS AND DISCUSSION

The synthetic route to well defined carbazol-3,9-diyl-based oligomers (6-8) is shown in Scheme 1. 3-[3,6-Di(*t*-butyl)carbazol-9'-yl]-9ethylcarbazole (6) was prepared via the modified Ullmann coupling [9] reaction of an excess of 3-iodo-9-ethylcarbazole (4) with 3,6-di (*t*-butyl)-9H-carbazole (2). The iodo-derivative 4 was prepared by alkylation of 3-iodo-9H-carbazole (3), which was synthesized by Tucker iodination [6] of 9H-carbazole (1). 3,6-Di(*t*-butyl)-9H-carbazole (2) was synthesized from 9H-carbazole(1) and *t*-butylchloride using Friedel-Crafts alkylation [5].









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Diphenylamino end-capped derivative with secondary amine function (5) was prepared by the modified Ullmann coupling reaction of 3-iodo-9H-carbazole (3) with a large excess of diphenylamine. The large excess of the amine had to be used in order to prevent polycondensation of 3-iodo-9H-carbazole. After the reaction an excess of diphenylamine was removed and the crude product 5 was treated with an excess of iodocompound, i.e. 3-iodo-9-ethylcarbazole or piodoanisole, respectively, by the Ullmann method, to provide ethylor methoxypheny- substituted oligo(carbazol-3,9-diyl)s with diphenylamino end-cap (7-8). All the compounds 6-8 were identified by mass spectrometry, IR and electronic absorption, as well as ¹H NMR spectroscopy. Transparent amorphous films of these materials can be prepared by vacuum deposition or spin coating from solutions.

Thermal properties of the materials **6–8** were examined by DSC and TGA. The TGA measurements revealed that the oligomers synthesized exhibited high thermal stability. The onset of decomposition for the materials occured above 360°C. Especially high thermal stability was observed for oligomer **7**, which has the highest molecular weight. The temperature of initial decomposition for **7** was 372° C, and 5% weight loss was observed at 421°C. All the materials were obtained as amorphous materials as confirmed by DSC (Figure 1). When samples of **6–8** were heated the glass-transitions were observed at 103°C for **6**, 154°C for **7** and at 123°C for **8**, and no peaks due to crystallization and melting appeared. Cooling down and the following repeated



FIGURE 1 DSC curves of the oligomers 6-8 at a heating rate of 10°C/min.

Compound	$\lambda_{\text{onset, Abs.}} (\text{nm})^*$	$\lambda_{\rm max, \ Fl.} \ ({\rm nm})^*$	$\lambda_{\rm max, \ Phos.} \ ({\rm nm})^{**}$	$E_{triplet} \; (eV)$
Cz	379	351	409	3.02
6	381	404	420	2.95
7	417	427	455	2.71
8	412	420	456	2.71

TABLE 1 Summary of Optical and Photophysical Characteristics of Cz and the Compounds **6–8**

*In thin film; **in ethanol at 77 K.

heating revealed only the glass transitions again. All the attempts to crystallize the compounds failed.

It should be mentioned that the materials synthesized exhibit fairly high glass transition temperatures, which are required to ensure the formation of morphologically stable, uniform, amorphous thin films. Such characteristics would render the devices using these materials more resistant against joule heating and gives rises to a higher current endurance. The more stable morphology would also reduce device degradation.

The optical and photophysical characteristics of the carbazole compounds are summarized in Table 1, in comparison with those of the unsubstituted carbazole (Cz). Carbazole has relatively the largest triplet energy $E_{triplet}$ of 3.02 eV (i.e., the transition energy of $T_1 \rightarrow S_0$ estimated from the highest-energy phosphorescence (Phos) peak at 409 nm). Carbazole derivatives **7–8** with larger conjugation compared to carbazole show a significant red shift in both fluorescence (Fl) $(\sim 70 \text{ nm})$ and phosphorescence $(\sim 45 \text{ nm})$, leading to a substantially lower triplet energy of 2.71 eV. In contrast, due to stronger localization of triplet wave functions, dimer $\mathbf{6}$ shows a much less lowering of the triplet energies, giving a triplet energy of 2.95 eV (420 nm). Such triplet energies would be large enough for applications in green or red phosphorescent OLEDs. The results shown in Table 1 also show that the 9th position of carbazole end-capped with phenyl substitution (i.e., 7 and 8) hardly has any effect on the photophysical characteristics, consistent with previous observations [10].

The compound **6** with the highest $E_{triplet}$ was used as host in phosphorescent OLEDs studies. The conducting polymer PEDT/PSS was used as the hole injection layer, a 40 nm NPD layer was used as the hole-transport layer and Alq₃ as the electron-transport layer. The thickness of Alq₃ layer was varied among devices from 30 nm to 50 nm. The emissive layer consisted of 20 nm of compound **6** doped with 6 wt.% of the green phosphor Ir(ppy)₃. A thin hole blocking layer

of 10 nm of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) was inserted between the emissive layer and the electron-transport layer to provide exciton and carrier confinement. The cathode consists of a thin LiF layer (0.5 nm) as the electron injection layer and a thick Al layer (150 nm) as the metal electrode.

Figure 2 compares the fluorescence and phosphorescence spectra of **6**, and the electroluminescence (EL) spectrum of the device. EL spectrum of the devices consisted entirely of the green emission of $Ir(ppy)_3$, and no emission from compound **6** was observed, indicative of complete energy transfer from compound **6** to $Ir(ppy)_3$. Such results are reasonable considering the high triplet energy of the host compound. Characteristics of the devices and external EL quantum efficiencies are shown in Figure 3. These OLEDs exhibit turn-on voltages of ~3.5 V (defined as the voltage where EL becomes detectable), external EL quantum efficiencies reaching 5% and maximum brightness of 11700 cd/m² (at 13 V). The maximal power efficiency was 7.2 lm/W. However, the devices show a gradual decrease of efficiency with increasing current, which is often observed in phosphorescent OLEDs and is usually attributed to triplet-triplet annihilation [11].

The device performances are promising, but not perfect yet, considering the host triplet energy to be as high as 2.95 eV. Such consequences are most probably due to imperfect carrier injection into the



FIGURE 2 Fluorescence and phosphorescence spectra of compound 6 and EL spectrum of device: $ITO/PEDOT-PSS/NPD/Ir(ppy)_3$ in material 6 host/BCP/ $Alq_3/LiF/Al$.



FIGURE 3 EL characteristics of devices: $ITO/PEDOT-PSS/NPD/Ir(ppy)_3$ in material 6 host/BCP/Alq₃/LiF/Al (with Alq₃ thickness of 30, 40 and 50 nm): (a) current density-voltage, (b) brightness-voltage, and (c) external EL quantum efficiency-current density.

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emission layer, as can be seen from the turn-on voltage, and probably also to the exciton quenching in adjacent layers of lower triplet energies due to exciton diffusion. It is believed that further optimization of the device structures (*e.g.*, carrier-transport layers, electrodes etc.) will further increase the device EL quantum efficiency.

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