

Donor-Substituted 1,3,5-Triazines as Host Materials for Blue Phosphorescent Organic Light-Emitting Diodes

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A series of new donor-substituted 1,3,5-triazines (TRZ 1–7) has been prepared by nucleophilic substitution of cyanuric chloride with carbazole, 3-methylcarbazole, phenol, and 3,5-dimethylphenol. These s-triazines have been investigated as host material for blue phosphorescent lightemitting diodes (OLEDs). All triazine based hosts were characterized regarding their optical and thermal properties. Different substitution patterns resulted in high glass-transition temperatures (T_{σ}) of up to 170 °C and triplet energies ($\Delta E(T_1 - S_0)$) of up to 2.96 eV. The application as host material for the blue phosphor bis(4,6-difluorophenylpyridinato-N,C2)picolinato-iridium(III) (FIrpic) yielded maximum current efficiencies up to 21 cd/A.

Introduction

Since the discovery of efficient phosphorescent emitters for organic light emitting diodes (OLED) by Forrest and Thompson many groups face the challenge to develop suitable new materials for phosphorescent OLEDs.^{1,2} In most small molecule-based OLEDs the emitting layer consists of a phosphorescent dye which is doped into a host material to avoid concentration quenching and to optimize the charge balance. High efficiencies are obtained only when the energy is efficiently transferred from the host the phosphorescent dye. For an efficient transfer the triplet energy of the host material has to be higher than that of the guest.³ This becomes more challenging for host materials used in combination with blue phosphorescent emitters, where triplet energies larger than 2.8 eV are required. In general, the electron mobility of many organic hosts is much lower than the hole mobility because of the fact that they mainly consist of strong electron donors like aromatic amines or carbazoles.⁴ In contrast, electron transport materials often contain electron deficient heterocycles. Triazines, for example, are known to be good electron conductors and therefore have

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been used as electron transport layer in OLEDs.⁵⁻⁷ However, the hole transport properties of most triazines are not sufficient for their use as host material in OLEDs. Recent developments of new matrix materials for phosphorescent organic light-emitting diodes often focus on the synthesis of bipolar materials.^{8,9} In a study by Inomata et al., donor-substituted 2,4,6-tris(diarylamino)-1,3,5-triazines were presented as matrix material and electron conductor for OLEDs.¹⁰ The combination of electron-accepting triazines and electron-donating diarylamine resulted in bipolar transport.¹¹ They proved to be a good host material for the green phosphorescent emitter tris(2-phenylpyridine)iridium $(Ir(ppy)_3)$. The highest triplet energy was presented for 2,4,6-tris(carbazolyl)-1, 3,5-triazine ($\Delta E(T_1-S_0) = 2.81$ eV). An OLED with 2,4,6-tris(carbazolyl)-1,3,5-triazine as host and Ir(ppy)₃ as guest have shown a maximum quantum efficiency of 10.2%.

Other OLED-relevant properties like the electrochemical properties of s-triazines¹² or the ab initio calculated molecular orbitals and triplet energies¹³ are described for this class of materials and show their potential as host materials for OLEDs. In a recent work, the electric field induced quenching on the phosphorescence intensity of a

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Scheme 1. Structures of the Donor-Substituted Triazines TRZ 1-7







deep-blue triplet emitter dispersed in a donor substituted triazine is described.¹⁴

TRZ 7

Another essential requirement for the successful operation of OLEDs, which is often neglected, is the ability of the material to form stable amorphous films.¹⁵ This property guarantees that the emitter stays uniformly diluted in the matrix to minimize the effect of concentration quenching. In addition, the absence of grain boundaries, which may act as trap states, makes the use of organic glasses as OLED materials advantageous.^{16,17} To obtain organic glasses, several points have to be taken into account. An important fact is to avoid strong intermolecular forces like hydrogen bonding or $\pi - \pi$ stacking between the molecules. Furthermore, the introduction of bulky substituents leads to a larger intermolecular distance and a hindrance in packing and therefore an amorphous behavior. On the other hand, the increased distance separates the conducting units from each other and results in decreasing charge carrier mobility. Another possibility to design organic glasses is the synthesis of asymmetric molecules. With this method, the number of conformers is increased and the high amount of energy

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In this paper, we describe the successful combination of high triplet energies and amorphous behavior for donor substituted triazines. This was achieved by the introduction of substituted carbazoles and the successive replacement of up to two carbazoles by phenoxy groups (Scheme 1). This yielded asymmetric materials with glasstransition temperatures up to 170 °C and triplet energies up to 2.96 eV. The device performance of **TRZ 2** as host materials for the blue phosphor FIrpic is presented.

Experimental Section

Materials. All commercially available reagents were purchased from Aldrich and used without further purification. The synthesis of tris[(3-phenyl-1H-benzimidazol-1-yl-2(3H)-ylidene)-1,2-phenylene]-Iridium (DPBIC) and 2,8-bis(triphenylsilyl)-dibenzo-furan (DBFSi) is described in the literature.^{19,20}

2,4,6-Tris(methylcarbazole-9'-yl)-1,3,5-triazine (**TRZ1**). **TRZ1** is a statistical mixture of a triazine core with 2- and 3-methylcarbazole substituents. A mixture of 2-methylcarbazole (1.45 g, 8.0 mmol) and 3-methylcarbazole (1.45 g, 8.0 mmol) was dissolved in dry THF (100 mL) under an argon atmosphere in a two-necked

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round-bottom flask equipped with a septum inlet and three way stopcock. n-Buthyllithium (1.6 M in hexane solution) (9.37 mL, 15 mmol) was added dropwise to the methylcarbazole solution and the mixture was stirred for 10 min. In a separate three-necked round-bottom flask equipped with a septum inlet, three-way stopcock, and condenser cyanuric chloride (0.83 g. 4.5 mmol) was dissolved in dry THF (60 mL) under argon. The carbazole-lithium solution was added dropwise to the cyanuric chloride solution using a transfer canula within 15 min. The reaction mixture was refluxed for 6 h. After the solution was cooled to room temperature, 40 mL of water were added. The product was filtered off; washed with water, hexane, and diethyl ether; and further prepurified by hot filtration from ethanol. Recrystallization from a chlorobenzene/hexane mixture vielded 1.7 g (61%) of **TRZ 1** as a white crystalline solid. ¹H NMR (250 MHz, d⁴-THF): δ (ppm) 8.96 (m, 6H), 8.02 (m, 6H), 7.31 (m, 9H), 2.53 (s, 4.3H), 2.38 (s, 4.7H). EI-MS: *m*/*z* 618 (100, M⁺), 309 (30, M²⁺).

2,4-Bis(carbazol-9'-yl)-6-chloro-1,3,5-triazine (1a). Carbazole (1.42 g, 8.5 mmol) was dissolved in dry THF (50 mL) under argon in a two-necked, round-bottom flask equipped with a septum inlet and three way stopcock. n-Buthyllithium (1.6 M in hexane solution) (5.0 mL, 8.0 mmol) was added dropwise to the methylcarbazole solution and the mixture was stirred for 10 min. In a separate three-necked, round-bottom flask equipped with a septum inlet, three-way stopcock, and condenser, cyanuric chloride (0.74 g, 4.0 mmol) was dissolved in dry THF (20 mL) in an argon atmosphere. The carbazole lithium solution was added dropwise to the cyanuric chloride solution using a transfer canula within 10 min. The reaction mixture was refluxed for 6 h. After the solution was cooled to room temperature, 40 mL of water was added. The product was filtered off: washed with water, hexane, and diethyl ether; and further purified by hot filtration from ethanol, to yield 1.2 g (68%) of 1a as a white crystalline solid. Mp: 231 °C. ¹H NMR (250 MHz, CDCl₃): δ (ppm) 8.92 (d, 4H), 8.06 (d, 4H), 7.56–7.40 (m, 8H). EI-MS: m/z 445 (100, M⁺), 192 (90), 166 (100).

2,4-Bis(3'-methylcarbazol-9'-yl)-6-chloro-1,3,5-triazine (1b). This compound was synthesized by a procedure similar to that of **1a** except that 3-methylcarbazole was used instead of carbazole. Yield: 1.5 g (78%) as a white solid. Mp: 235 °C. ¹H NMR (250 MHz, CDCl₃): δ (ppm) 8.81 (d, 2H), 8.66 (d, 2H), 7.92 (d, 2H), 7.72 (s, 2H), 7.41–7.33 (m, 4H), 7.22 (d, 2H), 2.50 (s, 6H). EI-MS: m/z 473 (100, M⁺), 237 (20, M²⁺), 180 (15).

2,4-Bisphenoxy-6-chloro-1,3,5-triazine (2). Cyanuric chloride (3.68 g, 20 mmol) was dissolved in acetone (200 mL) and cooled to 15 °C. In a separate flask, phenol (3.76 g, 40 mmol) was reacted with sodium hydroxide (1.60 g, 40 mmol) in water (200 mL). After the formation of the sodium phenolate was complete, the solution was cooled to 15 °C and added dropwise to the cyanuric chloride solution. The reaction mixture was stirred at temperatures below 15 °C for 8 h before 200 mL of water was added. The white precipitate was filtered and washed with water and ethanol. The product was purified by recrystallization from hexane to yield 5.8 g (85%) as white crystals. ¹H NMR (250 MHz, CDCl₃): δ (ppm) 7.42–7.35 (m, 4H), 7.28–7.22 (m, 2H), 7.13 (d, 4H). EI-MS: *m/z* 299 (100, M⁺).

2,4-Bis(carbazol-9'-yl)-6-phenoxy-1,3,5-triazine (**TRZ 2**). In a two-necked, round-bottom flask, 2,4-bis(carbazol-9'-yl)-6-chloro-1,3,5-triazine (**1a**) (0.89 g, 2 mmol) was dissolved in chloroform (20 mL). In a separate flask, phenol (0.23 g, 2.4 mmol) and sodium hydroxide (0.095 g, 2.4 mmol) were dissolved in 10 mL of water at room temperature and stirred for 10 min until the solution was added to the **1a**. Tetrabutylammonium bromide (12 mg, 0.04 mmol) and dibenzo-18-crown-6 (14 mg,

0.04 mmol) were added as phase-transfer catalysts. The mixture is heavily stirred for 8 h at 70 °C. After cooling of the solution to room temperature, addition of 20 mL of water, and extraction with diethyl ether, the organic phase was washed with water and dried over magnesium sulfate. The solvent was removed under reduced pressure and the product was purified by recrystallization from a hexane/THF mixture to yield 0.40 g (40%) of **TRZ 2** as a white crystalline solid. ¹H NMR (250 MHz, CDCl₃): δ (ppm) 8.74–8.70 (m, 4H), 8.04–8.00 (m, 4H), 7.60 (d, 2H), 7.44–7.36 (m, 11H). EI-MS: *m*/*z* 503 (100, M⁺), 337 (50), 166 (40).

2-(*Carbazol-9'-yl*)-4,6-bisphenoxy-1,3,5-triazine (**TRZ 3**). This compound was synthesized by a procedure similar to that of **1a** except that the ratio carbazole to triazine was 1.2 to 1. Yield: 0.77 g (90%) as white crystalline solid. ¹H NMR (250 MHz, CDCl₃): δ (ppm) 8.07 (d, 2H), 7.89 (d, 2H), 7.60–7.53 (m, 4H), 7.46–7.41 (m, 2H), 7.36–7.25 (m, 6H), 7.13–7.07 (m, 2H). EI-MS: *m/z* 430 (100, M+), 337 (100), 166 (50).

2,4-Bis(carbazol-9'-yl)-6-(3',5'-dimethylphenoxy)-1,3,5-triazine (**TRZ 4**). This compound was synthesized by a procedure similar as described for **TRZ 2**. 3,5-dimethylphenol was used instead of phenol. Yield: 0.92 g (86%) as a white crystalline solid. ¹H NMR (250 MHz, CDCl₃): δ (ppm) 8.78–8.74 (m, 4H), 8.05–8.01 (m, 4H), 7.41–7.29 (m, 8H), 7.09 (s, 1H), 7.04 (s, 2H), 2.44 (s, 6H). EI-MS: *m*/*z* 531 (70, M⁺), 365 (100), 166 (50), 105 (40).

2,4-Bis(3'-methylcarbazol-9'-yl)-6-phenoxy-1,3,5-triazine (**TRZ 5**). This compound was synthesized by a procedure similar as described for **TRZ 2**. Instead of 2,4-bis(carbazol-9'-yl)-6-chloro-1,3,5-triazine (**1a**) 2,4-bis(3'-methylcarbazol-9'-yl)-6-chloro-1,3, 5-triazine (**1b**) was used. Yield: 0.92 g (86%) as a white crystalline solid. ¹H NMR (250 MHz, CDCl₃): δ (ppm) 8.72–8.68 (m, 2H), 8.59 (d, 2H), 7.99–7.95 (m, 2H), 7.79 (s, 2H), 7.57 (d, 2H), 7.45–7.33 (m, 7H), 7.14 (d, 2H), 2.52 (s, 6H). EI-MS: *m*/*z* 531 (100, M⁺), 351 (30), 180 (30).

2,4-Bis(3'-methylcarbazol-9'-yl)-6-(3',5'-dimethylphenoxy)-1, 3,5-triazine (**TRZ 6**). This compound was synthesized by a procedure similar as described for **TRZ 2**. Instead 2,4-bis-(carbazol-9'-yl)-6-chloro-1,3,5-triazine (**1a**) 2,4-bis(3'-methylcarbazol-9'-yl)-6-chloro-1,3,5-triazine (**1b**) was used. 3,5-Dimethylphenol was used instead of phenol. Yield: 0.86 g (81%) as a white crystalline solid. ¹H NMR (250 MHz, CDCl₃): δ (ppm) 8.70–8.68 (m, 2H), 8.59 (d, 2H), 7.97–7.94 (m, 2H), 7.78 (s, 2H), 7.57 (d, 2H), 7.45–7.33 (m, 4H), 7.10 (s, 1H), 7.04 (s, 2H), 2.50 (s, 6H), 2.43 (s, 6H). EI-MS: *m*/*z* 559 (100, M⁺), 379 (50), 180 (35).

Bis(4,6-di(3'-methylcarbazol-9'-yl)-1,3,5-triazin-2-yl)resorcinol (**TRZ** 7). This compound was synthesized by a procedure similar to that described for **TRZ 2**. Instead of 2,4-bis(carbazol-9'-yl)-6-chloro-1,3,5-triazine (**1a**) 2,4-bis(3'-methylcarbazol-9'-yl)-6-chloro-1,3,5-triazine (**1b**) was used. Instead of phenol, resorcinol was used. The ratio of triazine to resorcinol to sodium hydroxide was changed to 1:2.4:2.2 (mmol). Yield: 0.47 g (48%) as a white solid. Mp: 300 °C. ¹H NMR (250 MHz, CDCl₃): δ (ppm) 8.74 (d, 4H), 8.58 (d, 4H), 7.93 (d, 4H), 7.74 (s, 4H), 7.60 (s, 1H), 7.50 (d, 2H), 7.42–7.25 (m, 9H), 7.21–7.13 (d, 4H), 2.49 (s, 12H). NMR. EI-MS: m/z 984 (100, M⁺), 804 (20), 492 (40, M²⁺), 180 (100).

Characterization. ¹H NMR spectra were recorded on a Bruker AC-250 spectrometer at 250 MHz. All NMR data given are given as chemical shifts δ (ppm) downfield from Si(CH₃)₄. MS spectra were obtained on a Finnigan Mat 8500, MAT 112 S Varian machine using EI-ionization. Melting points and glass-transition temperature determination was carried out on a Perkin-Elmer Diamond DSC at a heating/cooling rate of

10 K/min under a nitrogen atmosphere. Thermographimetric analysis (TGA) was performed on a Mettler Toledo TGA/ SDTA851e machine at a heating rate of 10 K/min in nitrogen atmosphere.

UV-vis absorption spectra were recorded on a Hitachi U-3000 spectrometer. Photoluminescence spectra were obtained using a Shimadzu Spectrofluorophotometer RF-5301PC. UVA-SOL solvents purchased from Merck were used to prepare solutions and films for optical characterization. The phosphorescence spectra were obtained with a time gated PL setup described elsewhere.¹⁴ In brief, thin film samples were mounted in a liquid helium coldfinger cryostat and excited by laser pulses (500 ps) at 337 nm. The detection of phosphorescence was accomplished by a gated microchannel-plate (MCP) with a time-gated detection window delayed with respect to the photoexciting pulse. For the experiments presented here, the detection started 500 ns after the pulse and for a time interval of 1 ms.

OLED Fabrication. The organic layers were deposited by thermal evaporation in high vacuum ($< 1 \times 10^{-6}$ mbar) onto indium—tin-oxide (ITO, 10 ohm/square) precoated glass substrates. Prior to use the ITO glass was degreased using organic solvents and cleaned using an UV-ozone oven for 30 min. The organic layers and the metal cathode were evaporated without breaking the vacuum.

Computational Calculations. The transport levels of the materials used were determined via density functional calculations. For the ionization potential and the electron affinity, first the geometry of the neutral as well as the charged states was optimized using the BP86-functional^{21,22} in combination with a split-valence basis set (SV(P)) including polarization functions on all heavy atoms.²³ For iridium, an effective core potential was employed.²⁴ For the energetics, single-point calculations at the optimized geometries using the same functional in combination with a valence triple- ζ basis set (TZVP)²⁵ were conducted. To account for dielectric solid-state effects, we used a UPS/IEPS-calibrated version of the conductor-like screening model (COSMO)²⁶ in conjunction with the single-point calculations. All calculations were carried out with the turbomole program package.²⁷

Results and Discussion

Synthesis. Previously reported 2,4,6-triscarbazolyl-1,3,5-triazine¹⁰ is highly crystalline with a melting point of 465 °C. Several attempts have been made to reduce the crystallinity of triscarbazolyl-triazines. The substitution of the s-triazine core with three 2-methylcarbazole units or three 3-methylcarbazoles still yielded materials with a high tendency to crystallize. Furthermore, we synthesized unsymmetrically substituted triscarbazolyl triazines. In a two-step synthesis, we were able to prepare various compounds with either two methylcarbazoles and one carbazole unit or three different methylcarbazole units. This strategy resulted in materials with slightly decreased crystallization tendencies. However, the glass formation

properties of these triazines were still poor. We found that a stoichiometric mixture of 2-methylcarbazole and 3-methylcarbazole (1:1) as substituents was the most effective way to obtain a less-crystalline material. **TRZ 1** is synthesized by nucleophilic substitution of cyanuric chloride with a 1:1 mixture of 2- and 3-methyl substituted carbazoles (see Scheme 2). The ¹H NMR spectrum of **TRZ 1** confirmed that the carbazoles are incorporated in an almost equimolar ratio.

The synthesis of the unsymmetrical triazines **TRZ 2** to TRZ 7 followed a different route. To obtain these compounds, at least two steps are required. For all materials except for TRZ 3, the first synthetic step was a substitution of cyanuric chloride with carbazole or 3-methylcarbazole. The number of carbazole substituents was controlled by the ratio of carbazole and triazine. This is possible because of the stepwise deactivation of the chlorine atoms at the triazine core after substitution with an electron donating carbazole unit. Therefore, the reaction can be efficiently stopped at this step and yields of 68% (1a) and 78% (1b) were obtained. In the second step, 1a and 1b were reacted with phenol and 3,5-dimethylphenol to yield triazines TRZ 2 and TRZ 5 as well as TRZ 4, and TRZ 6, respectively. In contrast to that, phenoxy substitutions mainly follow a temperature control.²⁸ The synthesis of intermediate 2 was carried out at temperatures below 15 °C to suppress the 3-fold substitution and yielded 85%. The substitution of 2 with carbazole yielded the triazine **TRZ 3**. For the synthesis of triazine **TRZ 7**, the diol resorcinol was reacted with 1b.

Thermal Characterization. The thermal properties of the novel triazines were investigated by differential scanning calorimetry (DSC), and their thermal stability was examined by thermogravimetric analysis (TGA). In both experiments, the heating and cooling rate was 10 K/min. The data are shown in Table 1. The first and second heating as well as the first cooling curves of **TRZ 1**, **TRZ 4**, and **TRZ 6** are shown in Figure 1.

All triazines exhibit a melting peak during the first DSC heating cycle. The melting temperatures range from 147 °C for TZR 5 to 335 °C for TRZ 1 (see Figure 1). TRZ 1, TRZ 2 and TRZ 3 crystallize upon cooling in the DSC. TRZ 4 forms a glass upon cooling and a glass transition can be observed in the subsequent heating cycle at 83 °C. On further heating, TRZ 4 crystallizes at 127 °C and exhibits a melting at 210 °C (see Figure 1). TRZ 5, TRZ 6 (see Figure 1), and TRZ 7 also form glasses on cooling. In contrast to TRZ 4, these triazines stay amorphous in the following heating and cooling cycles. The glass-transition temperatures of TRZ 5 (85 °C) and TRZ 6 (90 °C) are slightly higher than that of **TRZ 4**. The higher molecular weight of the dimeric compound TRZ 7 results in a much higher T_g of 170 °C. The thermal behavior can be reproduced in multiple cycles. The glass transition of TRZ 2 was determined in a separate experiment. The material was heated above its melting temperature and afterward

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Scheme 2. Synthesis of Donor-Substituted Triazines TRZ 1-7



TRZ3

Table 1. Thermal Properties of Triazines TRZ 1-TRZ 7 ^a							
product	$T_{\rm g}(^{\rm o}{\rm C})$	$T_{\rm m}$ (°C)	$T_{\rm c}(^{\rm o}{\rm C})$	$T_{\rm d}$ (°C)			
TRZ 1		335	295	372			
TRZ 2	80^b	219	135	356			
TRZ 3		248	186	307			
TRZ 4	83	210	127^{c}	310			
TRZ 5	85	147^{d}		364			
TRZ 6	90	171^{d}		386			
TRZ 7	170	301 ^d		399			

 ${}^{a}T_{g}$, glass-transition temperatures; T_{m} , melting temperatures; T_{c} , crystallization temperatures; and T_{d} , onset temperatures of decomposition or evaporation at ambient pressure. b Observed only after very fast cooling of the melt. c Observed only upon heating. d Observed only in the first heating scan.

cooled very fast using liquid nitrogen to yield a supercooled melt. On subsequent heating in the DSC, a T_g was observed at 80 °C followed by a crystallization peak at 121 °C and melting peak at 219 °C. However, it was not possible to observe a glass transition of **TRZ 1** and **TRZ 3** using this technique. These experiments demonstrate that it is possible to get stable glasses from these triazine compounds. All compounds exhibit a high thermal stability in the TGA experiment. The onset temperatures range from 307 to 399 °C for **TRZ 3** and **TRZ 7**, respectively (see Table 1). The evaporation temperatures in ultrahigh vacuum were found to be at least 50 °C below these temperature values for all materials. This high thermal stability enables thermal evaporation without decomposition. It was possible to yield amorphous films by spin coating or thermal evaporation from all triazine host materials. The films of **TRZ 1** and **TRZ 3** tended to crystallize after several hours to days. All other films were stable for at least 3 months (period of observation).

Optical Properties. The absorption, fluorescence, and phosphorescence spectra of TRZ 1-TRZ 3 films (thickness: 150 nm) on quartz are shown in Figure 2. The optical data for TRZ 1-3 are summarized in Table 2. The spectra show typical examples of triazines with three, two, and one carbazole group. The spectra of TRZ 4-TRZ 7 are very similar to those of TRZ 2 with a little bathochromic shift due to the inductive effect of the methyl groups attached to the carbazole. By comparing the absorption spectra of three triazines, it can be observed that the lowest energetic absorption maximum is shifted from 333 to 320 nm with an increasing amount of phenoxy substituents. From the absorption edge of these spectra, the optical bandgap can be estimated. TRZ 1 has the lowest bandgap of 3.54 eV. TRZ 2 and TRZ 3 have bandgap values of 3.61 and 3.75 eV, respectively. In the nongated room-temperature PL spectra, we observe the fluorescence of the compounds and the bathochromic shift is



Figure 1. First heating cycle (top line), second heating cycle (middle line), and first cooling cycle (bottom line) of TRZ 1, TRZ 4, and TRZ 6 (left to right).



Figure 2. Normalized absorption (left solid line), fluorescence (dotted line), and phosphorescence (right solid line) spectra of neat films of TRZ 1, TRZ 2, and TRZ 3 (top to bottom).

even more pronounced. The fluorescence of **TRZ 1** is relatively broad with a maximum at 385 nm. The spectrum of **TRZ 2** has two sharp peaks with almost the same height at 372 and 389 nm and a broad red-shifted shoulder. The fluorescence of **TRZ 3** is narrower with a maximum at 351 nm. The hypsochromic shift can be assigned to the electron withdrawing effect of the triazine on the single carbazole. In **TRZ 3**, the effect is very pronounced because only one carbazole unit is present. The hypsochromic shift becomes smaller in **TRZ 2** and **TRZ 1** with two and three carbazole units connected to the central triazine.

For the application as host material in OLEDs, the triplet level of the host must be higher compared to the guest. The triplet energy of selected triazines was determined from neat film time-gated phosphorescence spectra of neat films at T = 5 K. In this experiment, the detection of the phosphorescence spectrum is achieved by recording the PL several hundred nanoseconds after the laser pulse, i.e., after the prompt fluorescence has decayed

 Table 2. Photoluminescence Properties of Triazines TRZ 1–TRZ 3^a

product	$\lambda_{abs}(nm)$	$\begin{array}{c} \Delta E(\mathbf{S}_0 - \mathbf{S}_1) \\ (\mathrm{eV}) \end{array}$	$\lambda_{ m fluor}$ (nm)	$\lambda_{\rm phos}$ (nm)	$\begin{array}{c} \Delta E(\mathrm{T}_{1}\mathrm{-}\mathrm{S}_{0})\\ (\mathrm{eV}) \end{array}$
TRZ 1	285, 333	3.54	385	433, 465	2.86
TRZ 2	281, 330	3.61	372, 389	420, 450	2.95
TRZ 3	280, 308,	3.75	351	419, 450	2.96
	320				

 ${}^{a}\lambda_{abs}$, maxima of the absorption; $\Delta E(S_0-S_1)$, singlet bandgap, calculated form the edge of the absorption spectra; λ_{fluor} , maxima of the fluorescence; λ_{phos} , maxima of the phosphorescence; $\Delta E(T_1-S_0)$, triplet energy, calculated from the 0–0 phosphorescence transition.

and in the presence of the long-lived phosphorescence. The triplet energy was obtained from the first vibronic transition of the red-shifted phosphorescence spectrum. All spectra exhibited a vibronic progression up to the 0-2peak. **TRZ 1** shows a 0-0 phosphorescence transition at 433 nm (2.86 eV) and a maximum at 465 nm. Values of 420 nm (2.95 eV) and 419 nm (2.96 eV) for TRZ 2 and **TRZ 3** are determined for the respective 0-0 transitions. In contrast to the fluorescence, the difference of the first phosphorescence maximum of TRZ 2 and TRZ 3 is only 1 nm. These maxima are centered at 450 nm and correspond to the 0-1 transition. The weak signals between 320 and 400 nm may result from delayed fluorescence of the host materials as suggested by the good energy overlap with the prompt fluorescence spectra (dashed lines). From the high triplet energy values, it can be estimated that efficient exothermic energy transfer from all the presented TRZ host to blue phosphors such as FIrpic (2.65 eV) is possible.

Phosphorescent Organic Light-Emitting Diodes. Two OLEDs with the configurations shown in Figure 3 were fabricated to demonstrate the potential of donorsubstitued triazines as host material for blue phosphorescent emitters. For this purpose, TRZ 2 was chosen as representative material for this class. On top of indiumtin-oxide (ITO), poly(thiophene-3-[2-(2-methoxyethoxy)ethoxy]-2,5-diyl) was used as hole-injection layer followed by 35 nm of DPBIC p-doped with molybdenum(VI) oxide as hole-transporting layer. An additional 10 nm thick layer of DPBIC followed as exciton and electron blocker. The 20 nm thick emission layer consisted of TRZ 2 doped with 8% (device 1) or 16% (device 2) FIrpic. In device 1, **TRZ 2** was used as hole-blocking layer (5 nm) followed by 20 nm 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) as electron transporting material. In device 2, the hole-blocking and electron-conduction layers



Figure 3. Top: Electroluminescent spectra of device 1 and device 2 at 10 mA/cm². Bottom: Energy level diagram of device 1 and device 2; HOMO and LUMO levels of the different materials are indicated. The dotted lines represent the levels of the emitter FIrpic. The HOMO and LUMO levels were extracted from density functional theory (DFT) calculations.

consisted of 5 nm DBFSi and 40 nm BCP. The devices were finalized by deposition of LiF (0.7 nm)/Al (100 nm) cathode.

In the literature, the bipolar transport characteristics of a carbazol substituted triazine were reported.¹⁰ Therefore we consider it very important that exciton blocking layers are used on both sides of the emission layer. In our setup, DPBIC is used as exciton and electron blocker on the hole conduction side. The blocker on the electron conduction side was varied. In device 1, the host material **TRZ 2** itself was used. DBFSi, which was employed in device 2, acts both as effective hole and exciton blocker.

Figure 3 considers the electroluminescence spectra of both devices at a current density of 10 mA/cm^2 . Both spectra show a pure emission of FIrpic with a maximum at 473 nm and CIE coordinates of x = 0.17 and y = 0.32. Figure 4(top) displays the current density-voltageluminance characteristics of the devices. The device with **TRZ 2** as hole and excition blocking material (device 1) exhibted a 0.8 V lower turn-on voltage. This voltage increase can be attributed to the application of DBFSi as blocking layer which exhibits a higher LUMO level than TRZ 2 (see Figure 3). This results in an additional injection barrier. On the other side the current density and the luminance curves were steeper in device 2. Maximum luminances of 6900 and 1500 cd/m² were reached at 11 V for device 2 and device 1, respectively. The higher value of device 2 was attributed to the more effective exciton blocking of DBFSi. Figure 4(bottom) shows the external quantum efficiency (EQE) and current efficiency plotted versus the voltage. Here, the efficiency of the different blockers is even more pronounced. Device 2 exhibts a



Figure 4. Top: Luminance–voltage (solid symbols) and current–voltage (open symbols) characteristics of device 1 (circles) and device 2 (triangles). Bottom: External quantum efficiency–current density (solid symbols) and luminous efficiency–current density plots (open symbols) of device 1 (circles) and device 2 (triangles).

maximum EQE value of 10.2% at 22 cd/m². The maximum luminous and power efficiencies are 20.4 cd/A and 13.2 lm/W, respectively. At a luminesence of 100 cd/m², an EQE of 9.5% and a luminous efficiency of 19.2 cd/A were reached. The efficiencies of device 1 were significantly

lower. Maximum external quantum, luminous, and power efficiencies of 6.7%, 12.6 cd/A, and 8.7 lm/W were reached at 5.1, 5.1, and 4.4 V, respectively. These much lower values highlight the importance of a suitbale hole/exciton block-ing layer in this device setup. These results demonstrate the potential of donor-substituted triazines as host materials for blue phosphorescent OLEDs.

Conclusion

In this paper, we presented a series of new matrix materials based on the concept of donor-subbituted triazines with three, two, and one carbazole unit. The thermal properties, especially the glass formation, were controlled by different substitution patterns and amorphous host materials with glass-transition temperatures up to $170 \,^{\circ}$ C are obtained. This guarantees a long-term

morphological stability. The triplet energies of the triazines were in the range from 2.86 to 2.96 eV. The potential of this class of materials as hosts for blue phosphors has been tested. A maximum brightness of 6900 cd/m² and a maximum external quantum efficiency of 10.2% were reached using the blue emitter FIrpic. These first results show that the donor substituted of triazines hold great potential as host materials for blue OLEDs.

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