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Comparison of Tetraphenylmethane and Tetraphenylsilane as Core Structures of High-Triplet-Energy Hole and Electron-Transport Materials

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It is important to improve the quantum efficiency of organic light-emitting diodes (OLEDs) to reduce the power consumption of OLED displays. One effective approach to enhance the quantum efficiency of OLEDs is to adopt phosphorescent-emitting materials instead of the typical fluorescent-emitting materials.^[1] The use of a phosphorescent emitter could increase the external quantum efficiency of red, green, and blue OLEDs with more than 20 %.^[2–5]

To obtain high quantum efficiency in phosphorescent OLEDs (PHOLEDs), it is important to confine triplet excitons and charges inside the emitting layer.^[3–9] For this purpose, hole- and electron-transport layers play an important role. Therefore, the hole- and electron-transport materials should have higher triplet energy than the phosphorescent emitters and should have the energy levels for hole or electron blocking. In particular, the triplet energy of the hole- and electron-transport materials should be above 2.80 eV for applications in all red, green, and deep-blue PHOLEDs.^[5,6]

The most popular approach to get high triplet energy in charge-transport materials is to separate the conjugated building units to reduce the conjugation length of the molecule.^[5,7–9,10–16] Typically, tetraphenylsilane with silicon as the linking unit has been widely used as core structures for high-triplet-energy, charge-transport materials, because silicon disconnects the conjugation between different building units.^[5,10-13] Several materials with tetraphenylsilane as core structures have been developed for applications as high-triplet-energy, hole- and electron-transport materials. For example, diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSPO1) is effective as a high-triplet-energy, electron-transport material for all red, green, and deep-blue PHOLEDs^[5] and 2,5-bis(4-triphenylsilanyl-phenyl)^[1,3,4] oxadiazole can be used as electron-transport material for green PHOLEDs.[11] For hole-transport materials, bis[4-(p,p'-ditolylamino)phenyl]diphenylsilane improves the external quantum efficiency of sky-blue PHOLEDs.^[10]

In addition to the tetraphenylsilane, tetraphenylmethane, with sp³-type carbons as the linking unit to separate the aromatic building units, has also been used as high-tripletenergy core, because sp³ carbons have a tetragonal geometrical structure. However, there have been few reports on tetraphenylmethane as core structures of high-triplet-energy, hole- and electron-transport materials, although several compounds with sp³ carbons in the fused ring structure are known.^[17,18]

Herein, two high-triplet-energy, hole-transport materials, with tetraphenylmethane and tetraphenylsilane core structures, and one high-triplet-energy, electron-transport material, with a tetraphenylmethane core, are described and the roles of tetraphenylmethane and tetraphenylsilane as building units are compared. Tetraphenylmethane show good performance as the core structure of hole-transport materials, whereas tetraphenylsilane is effective as the core of electron-transport materials.

Four hole- and electron-transport materials were prepared to compare tetraphenylsilane and tetraphenylmethane as core structures of charge-transport materials. Two holetransport materials, *N*,*N*-diphenyl-4-(triphenylsilyl)aniline (TSPA) and *N*,*N*-diphenyl-4-tritylaniline (TCPA), with tetraphenylsilane and tetraphenylmethane core structures, respectively, were modified with a diphenylamine functional group to obtain good hole-transport properties. Two electron-transport materials, TSPO1 and diphenyl(4-tritylphenyl)phosphine (TCPO1), have the same backbone structure and were modified with a diphenylphosphine oxide functional group to improve the electron-transport properties. The synthesis of the TSPO1 has been reported in our previous work.^[5] The other compounds were newly synthesized in this work.

The synthesis of the three charge-transport materials is shown in Scheme 1. TSPA was easily prepared by the amination of brominated tetraphenylsilane by using palladium(II)acetate as the catalyst. TCPA was synthesized by the reaction of tritylaniline with bromobenzene with palladium(II)acetate as the catalyst. TCPO1 was synthesized by the phosphorylation of 1-bromo-4-tritylbenzene prepared from 4-tritylaniline. All compounds were purified by column chromatography to obtain a purity level above 99% from high-performance chromatography analysis. The detailed synthesis of the compounds is described in the Supporting Information.

Chem. Eur. J. 2012, 00, 0-0

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These are not the final page numbers! **77**

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201103640.



Scheme 1. Synthesis TCPA, TSPA, and TCPO1. The chemical structure of TSPO1 is also shown.

Photophysical properties of the four charge-transport materials were measured with UV/Vis and photoluminescence (PL) spectrometers. Table 1 summarizes the UV/Vis and PL data of the four compounds and the spectra are presented in the Supporting Information (Figure S1). TSPA and TCPA showed strong UV/Vis absorption signals at 309 and 304 nm, respectively, due to the strong absorption of the diphenylamine unit. The UV/Vis absorption was redshifted by 5 nm for TSPA, with the tetraphenylsilane core. The PL emission

Table 1. Physical properties of charge-transport materials.

Material	UV/Vis [nm] ^a	PL [nm] ^[a]	HOMO [eV] ^[b]	LUMO [eV] ^[c]	Bandgap [eV] ^[d]	Triplet Energy [eV] ^[e]
TCPA	304	366	-5.78	-2.11	3.67	2.92
TSPA	309	371	-5.82	-2.26	3.56	2.90
TCPO1	272	324	-6.75	-2.29	4.46	3.38
TSPO1	278	322	-6.79	-2.52	4.27	3.36

[a] Measured in tetrahydrofuran. [b] HOMOs were measured by CV. [c] LUMOs were calculated from the difference between HOMO and bandgap. [d] Bandgaps were calculated from the absorption edges of the UV/Vis spectra. [e] Triplet energies were calculated from the first emission peaks of low-temperature PL spectra. of TSPA was similarly redshifted by 5 nm compared with that of TCPA, due to the redshifted UV/Vis absorption. The bandgaps could be calculated from the absorption edges of the UV/Vis spectra and they were 3.56 and 3.67 eV for TSPA and TCPA, respectively. The redshifted absorption/ emission spectra and the reduced bandgap of TSPA can be explained by the LUMO stabilization effect of the silicon unit in the tetraphenylsilane core.^[19-21] Although both carbon and silicon are known to separate the conjugation of the aromatic group, silicon tends to extend the LUMO of the conjugated molecule because the σ^* orbital of silicon interacts with the π^* orbital of the conjugated unit. As the HOMO is not greatly affected by the silicon linking group, the LUMO of the silicon-based molecule is stabilized, leading to a reduced bandgap and redshifted emission. In the case of carbon, it does not affect the HOMO and LUMO of the molecules because the conjugation is completely isolated by the sp³ carbons. This is confirmed by the HOMO/LUMO levels of TCPA and TSPA. There is little difference between the HOMO levels of TCPA and TSPA, whereas the LUMO is stabilized by 0.15 eV in TSPA. Similar results were obtained for the TCPO1 and TSPO1. Redshifts of the UV/Vis absorption and PL emission signals were observed and the



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bandgap is decreased in TSPO1, containing the silicon unit. The LUMO is most stabilized in TSPO1 due to the silicon unit, leading to a reduced bandgap.

The triplet energy of the four compounds was calculated from the first emission peak of low-temperature (77 K) PL spectra. The triplet energies of TSPA and TCPA are 2.90 and 2.92 eV, whereas those of TSPO1 and TCPO1 are 3.36 and 3.38 eV, respectively. Tetraphenylsilane-based, chargetransport materials exhibit lower triplet energy than the tetraphenylmethane-based material due to the extended conjugation. All four charge-transport materials show triplet energy high enough for exciton blocking in deep-blue PHOLEDs.

The HOMO and LUMO levels of the four materials were measured by cyclic voltammetry (CV) and are summarized in Table 1. The HOMO level of TCPA is -5.78 eV, whereas that of TSPA is -5.82 eV. There is only 0.04 eV difference between the HOMO levels of the two hole-transport materials. However, the LUMO level is lowered by 0.15 eV in TSPA due to the LUMO stabilization effect explained above. The HOMO and LUMO levels of TCPA and TSPA are suitable for hole injection and electron blocking in deepblue PHOLEDs.

TCPO1 and TSPO1 show deep HOMO levels of -6.75 and -6.79 eV, and LUMO levels of -2.29 and -2.52 eV due to the electron-withdrawing phosphine oxide unit. As the bandgap of the two electron-transport materials is large, because the conjugation is isolated by phosphine oxide unit, the LUMO levels are rather high.

The thermal stability of TCPA, TSPA, and TCPO1 was analyzed by using a thermogravimetric analyzer and all three compounds were stable up to 350°C (Figure S2 in the Supporting Information).

Molecular simulation of the four materials was carried out to correlate the molecular-orbital distribution with photophysical properties of the materials. A suite of the Gaussian 03 program and the nonlocal density functional of Becke's 3-parameters employing the Lee-Yang-Parr functional (B3LYP) with the 6-31G* basis sets were used for the simulation.^[22] Figure 1 shows the HOMO and LUMO distribution of the four materials. The HOMOs of TCPA and TSPA are localized on the triphenylamine unit, whereas the LUMOs are dispersed over the whole molecule. There was little difference of the HOMO and LUMO distribution between TCPA and TSPA. In the case of TCPO1 and TSPO1, the LUMOs are distributed over the phenyl unit connected to the diphenylphosphine oxide, whereas the HOMOs are dispersed over the phenyl units attached to the carbon or silicon atoms, due to the strong electron-withdrawing character of the diphenylphosphine oxide. The HOMO and LUMO distributions of TCPO1 and TSPO1 are similar. The carbon and silicon atoms do not induce significant change to the molecular-orbital distribution. Therefore, the HOMO and LUMO difference between carbon and silicon compounds originates from the LUMO stabilization effect of silicon.

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Figure 1. Molecular-simulation results of TCPA, TSPA, TCPO1, and TSPO1.

To compare tetraphenylmethane and tetraphenylsilane as core structures of high-triplet-energy, hole-transport materials, hole-only devices of TCPA and TSPA were fabricated. The structure of the hole-only devices was as follows: indium tin oxide (ITO, 50 nm)/N,N'-diphenyl-N,N'-bis-[4-(phenyl-m-tolyl-amino)-phenyl]-biphenyl-4,4'-diamine

(DNTPD, 60 nm)/N, N'-di(1-naphthyl)-N, N'-diphenylbenzidine (NPB, 5 nm)/TSPA or TCPA (30 nm)/Au. Figure 2a shows the current density of hole-only devices of TCPA and TSPA. The hole current density of TCPA was higher than that of TSPA, indicating that TCPA is better than TSPA as a hole-transport material. Because of the small differences (0.04 eV) between the HOMO levels of TCPA and TSPA, the high hole current density of TCPA can be explained by the better hole-transport properties of TCPA. In the molecular-orbital diagram, the HOMO is dispersed over the triphenylamine unit in both materials and is little affected by the linking unit, indicating that the different hole-transport properties are not caused by the HOMO distribution. Instead, the different hole-transport properties can be explained by the molecular size of TCPA and TSPA. The length of the carbon-carbon bond is shorter than that of carbon-silicon and the atomic size of carbon is smaller than that of silicon, indicating that the tetraphenylmethane core is smaller than the tetraphenylsilane core. Therefore, the intermolecular packing is improved in TCPA, leading to better hole-transport properties.^[23]

Electron-only devices of TCPO1 and TSPO1 were fabricated to compare tetraphenylmethane and tetraphenylsilane as core structures of high-triplet-energy, electron-transport materials. The device structure was as follows: ITO (50 nm)/ LiF (1 nm)/TSPO1 or TCPO1 (50 nm)/LiF (1 nm)/Al (200 nm). Data for the electron-only devices of TCPO1 and TSPO1 are shown in Figure 2b. The electron current density was much higher in TSPO1 than in TCPO1. In contrast to the data of the hole-only device, tetraphenylsilane was better than tetraphenylmethane regarding electron trans-



500

450

400

350

300

250

200

150

100

50

0 4

Current density (mA cm⁻²)



1

6

2

port. On the basis of the molecular size, TSPO1 should be worse than TCPO1, because TCPO1 possesses short carbon-carbon bonds. However, TSPO1 show high electron current density. This can be explained by differences in LUMO levels and molecular-orbital distributions between TCPO1 and TSPO1. The LUMO level of the electron-transport material is critical for the electron injection. The LUMO level of TSPO1 (-2.52 eV) is more suitable, than that of TCPO1 (-2.29 eV), for electron injection from a LiF/Al electrode to the electron-transport layer, because of smaller energy barriers for electron injection. The reduced energy barrier facilitates electron injection from the LiF/Al cathode to TSPO1. The extended LUMO dispersion of TSPO1 also contributes the high electron current density of TSPO1. The extended LUMO distribution facilitates electron transport and improves the electron current density of TSPO1. In the case of TCPO1, all phenyl units in the molecule are separated; this has a negative effect on the electron transport.

Deep-blue PHOLEDs were fabricated by using tetraphenylmethane- and tetraphenylsilane-based, hole- and electron-transport materials. The device structure was as follows: ITO (50 nm)/DNTPD (60 nm)/NPB (5 nm)/TSPA or TCPA (30 nm)/(9-(3-(9H-carbazol-9-yl)phenyl)-9H-carbazol-3-yl)diphenylphosphine oxide: bis((3,5-difluoro-4-cyanophenyl)pyridine) iridium picolinate (30 nm, 3%)/TSPO1 or TCPO1 (25 nm)/LiF (1 nm)/Al (200 nm). Figure 3 shows the current density–voltage–luminance and quantum efficiency– luminance curves of deep-blue PHOLEDs. The current density of the deep-blue PHOLEDs is maximized in the device



Figure 3. a) Current density-voltage-luminance and b) quantum efficiency-luminance data of deep-blue PHOLEDs with different hole- and electron-transport materials: TCPA/TSPO1 (\bullet), TSPA/TSPO1 (\bullet), TCPA/TCPO1 (\bullet), TCPA/TCPO1 (\bullet).

with TCPA and TSPO1 as hole- and electron-transport layers; this is in agreement with the hole-only and electrononly device data. The deep-blue PHOLED with TSPA and TCPO1 shows the lowest current density. The luminance followed the same tendency as the current density in the different hole- and electron-transport materials. The TCPA/ TSPO1 deep-blue PHOLED also exhibited higher quantum efficiency than other devices, because of better charge balance in the emitting layer. Other devices were not as good as the TCPA/TSPO1 device, due to unbalanced hole and electron injection.

In conclusion, tetraphenylmethane and tetraphenylsilane were compared for the use as building units in hole- and electron-transport materials. Tetraphenylmethane works effectively as building units of hole-transport materials, whereas tetraphenylsilane is a good building unit in electron-transport materials. Therefore, the combination of tetraphenylmethane-based, hole-transport materials and tetraphenylsilane-based, electron-transport materials gives the best performances in deep-blue PHOLEDs.

Keywords: deep-blue PHOLEDs • high triplet energy • hole transport material • tetraphenylmethane • tetraphenylsilane

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Received: November 18, 2011 Revised: February 28, 2012 Published online: ■■ ■, 0000



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Comparison of Tetraphenylmethane and Tetraphenylsilane as Core Structures of High-Triplet-Energy Hole and Electron-Transport Materials



Tetraphenylmethane and tetraphenylsilane were compared as building units for high-triplet-energy, charge-transport materials. Tetraphenylsilane is effective as the building unit in electron-transport materials, whereas tetraphenylmethane is suitable in holetransport materials (see figure; TSPO1 = diphenylphosphine oxide-4-(triphenylsilyl), TSPA = phenyl-N,Ndiphenyl-4-(triphenylsilyl)aniline, and TCPA = N,N-diphenyl-4-tritylaniline).