Bridged triphenylamines as novel host materials for highly efficient blue and green phosphorescent OLEDs†

Zuoquan Jiang,[a] Yonghua Chen,[b] Cong Fan,[a] Chuluo Yang,*[a] Qi Wang,[b] Youtian Tao,[a] Zhiqiang Zhang,[b] Jingui Qin[a] and Dongge Ma*[b]

Received (in Cambridge, UK) 11th February 2009, Accepted 25th March 2009
First published as an Advance Article on the web 27th April 2009
DOI: 10.1039/b902950h

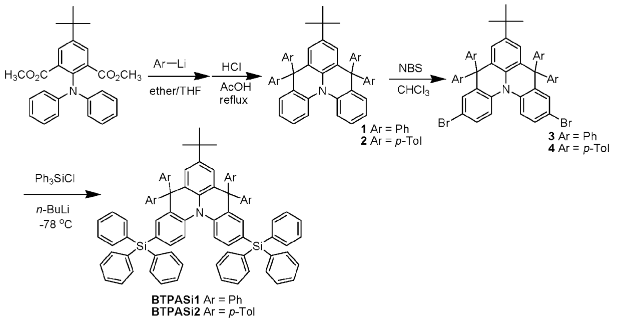
Two bridged triphenylamine–triphenylsilane (BTPASi) hybrids have been designed as host materials for phosphorescent OLEDs; devices with the novel host materials achieve maximum external quantum efficiencies as high as 15.4% for blue and 19.7% for green electrophosphorescence.

Phosphorescent organic light-emitting diodes (PHOLEDs) have attracted intense interest because they can in theory approach 100% internal quantum efficiency.[1] The triplet emitters of heavy-metal complexes are normally doped in a host matrix to reduce concentration quenching and triplet–triplet annihilation *etc.*,[2] and thus a suitable host material for separation of the triplet emitters is vital to achieve efficient electrophosphorescence. The host for phosphorescent emitters has to fulfil the requirement that the triplet energy of the host has to be higher than that of the guest. This should prevent reverse energy transfer from the guest back to the host and confine triplet excitons to the guest molecules.[3] This requirement still remains a challenge in designing a host for blue electrophosphorescence because one should avoid extended conjugation to achieve a high triplet energy; on the other hand, a bulky and sterically hindered molecular configuration is preferable for forming morphologically stable and uniform amorphous films.[4] Up to now, the hosts for blue electrophosphorescence are mainly focused on carbazole-based derivatives, such as 4,4′-bis(9-carbazolyl)-2,2′-biphenyl (CBP),[1b] 1,3-bis(9-carbazolyl)benzene (*m*CP),[3b] 3,5-bis(9-carbazolyl)-tetraphenylsilane (SimCP),[5a] 9-(4-*tert*-butylphenyl)-3,6-bis-(triphenylsilyl)-9*H*-carbazole (CzSi), *etc.*[5b] In addition, a series of organosilicon compounds with ultrahigh energy gaps as host materials for deep blue electrophosphorescence have also been reported.[3d–e,6]

As we know, triphenylamine (TPA) has a high triplet energy of 3.04 eV[7] and good hole-transporting abilities.[8] These characteristics mean that TPA derivatives are close to meeting the desired criteria for a host material; however, the flexible TPA molecules lack rigidity, which is disadvantageous to its thermal and morphological stabilities, and consequently limits its application as host material in OLEDs. So far, there are very few triphenylamine-based host materials. Recently, Shu's group reported a high triplet energy host based on a TPA–fluorene hybrid for efficient blue (18.1 lm W^{-1}, 13.1%) and green (21 lm W^{-1}, 12%) electrophosphorescence.[9] We also reported a TPA–oxadiazole derivative as bipolar host for red electrophosphorescence (8.2 lm W^{-1}, 14.2%).[10]

In our search for new high triplet energy materials capable of hosting blue-emitting phosphors, the rigidity of the carbazole structure, as well as the high triplet energy and good hole-transporting ability of triphenylamine, inspired us to design a rigid triphenylamine skeleton. Towards this aim, we synthesized a bridged triphenylamine *via* a diarylmethene linkage between two phenyl rings. To have a large energy gap and molecular size simultaneously, the electrochemically active sites (*para* position of the nitrogen) of TPA were blocked with triphenylsilyl through the non-conjugated sp^3-hybridized silicon atom.[5b] The bulk and steric spacer triphenylsilyl, as well as the aryl substituents on the bridgehead carbon atom, are expected to effectively separate the triplet guest molecules, and improve their thermal and morphological stabilities. The new hosts retain the high triplet energy (*ca.* 2.96 eV) of TPA. Devices fabricated with the new hosts show maximum external quantum efficiencies as high as 15.4% (35 lm W^{-1}) for blue and 19.7% (64 lm W^{-1}) for green electrophosphorescence.

The new hosts were synthesized according to the synthetic route shown in Scheme 1. The initial intermediate 5-*tert*-butyl-2-diphenylamino-isophthalic acid dimethyl ester was treated with aryllithium, and subsequently underwent intramolecular ring closure through Friedel–Crafts reaction to give the bridged triphenylamines (BTPA). The BTPAs were



Scheme 1 Synthesis of BTPASi1 and BTPASi2.

---

[a] Department of Chemistry, Hubei Key Lab on Organic and Polymeric Optoelectronic Materials, Wuhan University, Wuhan, 430072, PR China. E-mail: clyang@whu.edu.cn; Fax: +86 27-68756757; Tel: +86 27-68756757
[b] State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, PR China. E-mail: mdg1014@ciac.jl.cn; Fax: +86 431-85262357; Tel: +86 431-85262357

† Electronic supplementary information (ESI) available: Synthesis, characterization, crystal structure of the compounds. CCDC 714843. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b902950h

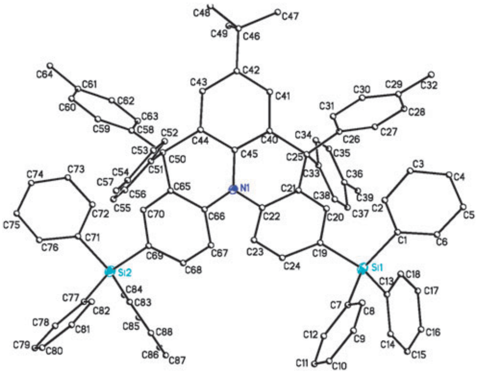


Fig. 1 Molecular diagram of BTPASi2 (for clarity, non-carbon atoms are shown with 30% thermal ellipsoids probability; carbon atoms are shown as spheres; hydrogen atoms and solvent molecules are omitted).

brominated with NBS under mild conditions, and the obtained dibromo-BTPAs were treated with *n*-BuLi at −78 °C, and then quenched with chlorotriphenylsilane to afford the desired products BTPASi1 and BTPASi2. All the compounds were fully characterized by ^{1}H NMR, ^{13}C NMR, mass spectrometry, and elemental analysis (see ESI†). Furthermore, the molecular structure of BTPASi2 was determined by X-ray single-crystal crystallographic analysis.‡ As shown in Fig. 1, the molecule displays a three-dimensional scissor-like conformation, which should be advantageous in effectively isolating the triplet guest molecules, and suppress the intermolecular aggregation.[11]

The good thermal stability of the compounds is indicated by the high decomposition temperatures (T_d, corresponding to 5% weight loss, see Table 1) of 483 °C for BTPASi1 and 491 °C for BTPASi2 in thermogravimetric analysis. Their glass transition temperatures (T_g) were observed at 168 °C for BTPASi1 and 173 °C for BTPASi2, through differential scanning calorimetry (DSC), which are much higher than those of triphenylamine analogues, such as 1,4-bis[(1-naphthylphenyl)amino]biphenyl (NPB, 98 °C), as well as carbazole analogues, such as CBP (62 °C) and *m*CP (60 °C).[12] The high T_g and T_d values of the two compounds may be mainly attributed to the rigid bridged TPA core, and can improve the film morphology and reduce the possibility of phase separation upon heating.

BTPASi1 and BTPASi2 show almost the same electronic absorption and fluorescence spectra (Fig. 2). The absorption at 328 nm may be attributed to π–π* transitions of the bridged-triphenylamine core. Their PL spectra in CH_2Cl_2 solution exhibit ultraviolet emission at *ca.* 370 nm. Their emission maxima in the film are only red-shifted by 2–4 nm with respect to their CH_2Cl_2 solutions (Fig. S2†), which implies that the triphenylsilyl moiety, as well as the peripheral aryl group on the bridgehead carbon atom, effectively suppresses intermolecular aggregation.[13] The inset of Fig. 2 depicts the phosphorescence spectra of BTPASi1 and BTPASi2 measured on a frozen toluene matrix at 77 K. Their triplet energies (E_T) were determined to be *ca.* 2.95 eV by the highest-energy vibronic sub-band of the phosphorescence spectra. This value is sufficiently high to host red, green, and blue phosphorescent emitters, such as the common blue-emitter bis[2-(4′,6′-difluorophenyl)pyridinato-*N*,$C^{2'}$]iridium(III) picolate (FIrpic, 2.62 eV) and green-emitter iridium(III) *fac*-tris(2-phenylpyridine) ($Ir(ppy)_3$, 2.42 eV).

Table 1 Thermal and optical properties of BTPASi1 and BTPASi2

	T_d/°C	T_g/°C	Abs λ_{max}/nm soln^a/film	PL λ_{max}/nm soln^a/film	$E_T{}^b$/eV
BTPASi1	483	168	328/329	370/374	2.95
BTPASi2	491	173	328/331	369/371	2.97

^{a} Measured in CH_2Cl_2 solution. ^{b} Triplet energy.

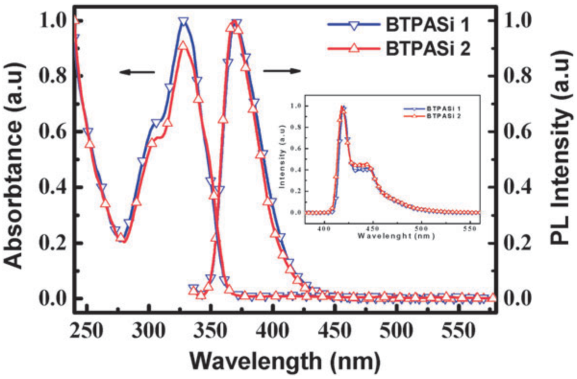


Fig. 2 Absorption and emission spectra of BTPASi1 and BTPASi2 in CH_2Cl_2 solution at room temperature, and their phosphorescence spectra in toluene at 77 K (inset).

The electrochemical behaviours of BTPASi1 and BTPASi2 were probed by cyclic voltammetry (CV). They all exhibit a reversible oxidation process. Further more, upon repeated scanning, both still show reversible oxidation behavior. This contrasts with the irreversible oxidation process of the pristine triphenylamine.[14] Such electrochemical reversibility can be attributed to the blocking of the three *para*-phenyl position active sites by the *tert*-butyl and triphenylsilyl moieties, and should benefit the stability of their electroluminescence devices.

We investigated the utility of BTPASi1 and BTPASi2 as the host materials for blue and green phosphorescent devices with the following configurations: device A–B: ITO/MoO_3(10 nm)/NPB(80 nm)/*m*CP(5 nm)/host: FIrpic(20 nm)/3-(4-biphenylyl)-4-phenyl-5-(4-*tert*-butylphenyl)-1,2,4-triazole (TAZ, 40 nm)/LiF/Al; device C–D: ITO/MoO_3(10 nm)/NPB(80 nm)/*m*CP(5 nm)/host: $Ir(ppy)_3$(20 nm)/TAZ(40 nm)/LiF/Al. NPB was used as the hole-transporting material; *m*CP was used to confine excitons to the emitting layer; TAZ was used as electron-transporting as well as hole-blocking material;[3e] phosphors FIrpic and $Ir(ppy)_3$ doped in the host were used as the emitting layer, with optimized doping levels of FIrpic and $Ir(ppy)_3$ at 6% and 9%, respectively; MoO_3 and LiF served as hole- and electron-injecting layers, respectively.[15] The luminance–current density–current efficiency (L–J–η_c) characteristics of the devices are shown in Fig. 3. The device data are summarized in Table 2.

Device A with BTPASi1 as host and FIrpic as dopant exhibits a maximum current efficiency of 44 cd A^{-1}, a maximum power efficiency of 35 lm W^{-1}, and a maximum luminance of 6543 cd m^{-2}. At the practical brightness of 100 cd m^{-2}, the current efficiency is still as high as 36.5 cd A^{-1}. To the best of our knowledge, the device efficiencies are among the highest for the blue phosphorescent OLEDs to date.[5b,9]

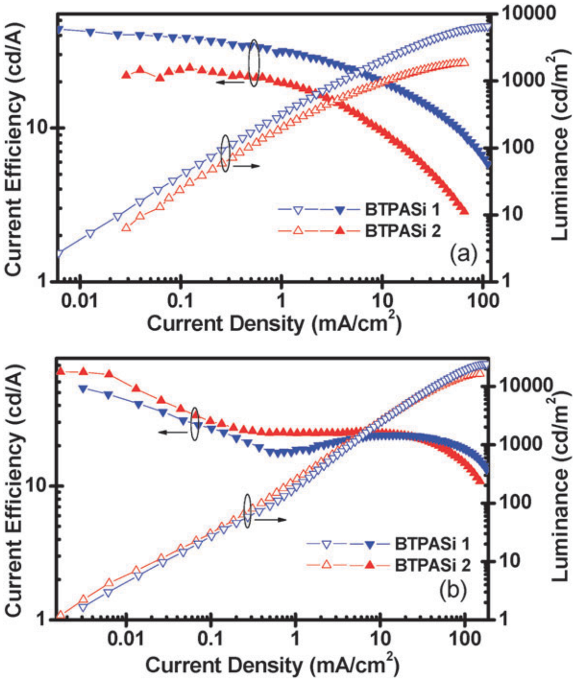


Fig. 3 Current efficiency (η_c)/luminance (L) *versus* current density (J) (a) for the FIrpic based devices; (b) for the Ir(ppy)$_3$ based devices.

Table 2 Summary of device performance

Host	BTPASi1		BTPASi2	
Dopant	FIrpic	Ir(ppy)$_3$	FIrpic	Ir(ppy)$_3$
Device	A	C	B	D
$V_{\text{turn-on}}$/V	3.9	3.7	3.7	3.5
L^a/cd m^{-2}	6543	24 029	1865	16 473
EQE^b (%)	15.4	15.0	8.8	19.7
LE^c/cd A^{-1}	44	54	25	71
PE^d/lm W^{-1}	35	46	17	64
CIE (x, y)	(0.26, 0.48)	(0.33, 0.60)	(0.26, 0.47)	(0.33, 0.60)

[a] Maximum luminance. [b] Maximum external quantum efficiency. [c] Maximum current efficiency. [d] Maximum power efficiency.

Device D with BTPASi2 as host and Ir(ppy)$_3$ as dopant shows a maximum current efficiency of 71 cd A^{-1}, a maximum power efficiency of 64 lm W^{-1}, and a maximum luminance of 16 473 cd m^{-2}. We note that the efficiencies are comparable with the best green phosphorescent OLEDs we recently reported.[2c]

In summary, we have designed a type of bridged triphenylamine–triphenylsilane (BTPASi) hybrids as novel host materials for phosphorescent OLEDs. The rigidification of triphenylamine significantly improves their thermal and morphological stabilities without affecting their good hole-transporting ability and high triplet energy. Devices with the host materials show maximum external quantum efficiency as high as 15.4% for blue and 19.7% for green electrophosphorescence. This work reveals a very promising application of triphenylamine-based derivatives as efficient host materials. The further optimization of device configuration is under way.

We thank the National Natural Science Foundation of China (Project Nos. 50773057, 20474047 and 20621401), the Ministry of Science and Technology of China through the 973 program (Grant Nos. 2009CB623602, 2009CB930603, 2009CB623604) for financial support.

Notes and references

‡ Crystal data of BTPASi2 at 293(2) K: $C_{92}H_{83}NO_2Si_2$, M_r = 1290.77, monoclinic, space group $P2_1/c$, D_c = 1.144 g cm^{-3}, Z = 4, a = 14.6954(5) Å, b = 19.5226(5) Å, c = 26.3298(9) Å, α = 90°, β = 97.2890(10)°, γ = 90°, V = 7492.8 (4) Å^3, μ = 0.097 mm^{-1}. Bruker AXS Smart CCD diffractometer, Mo-Kα radiation, λ = 0.71073 Å, number of reflections measured = 59 952, number of independent reflections = 13 230, R_{int} = 0.0746, final $R(F)$ = 0.0659 ($I > 2\sigma(I)$), w$R(F^2)$ = 0.1657. CCDC 714843.

1 (*a*) M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, M. E. Thompson and S. R. Forrest, *Nature*, 1998, **395**, 151; (*b*) M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson and S. R. Forrest, *Appl. Phys. Lett.*, 1999, **75**, 4; (*c*) X. Yang, D. C. Müller, D. Neher and K. Meerholz, *Adv. Mater.*, 2006, **18**, 948; (*d*) G. Zhou, W.-Y. Wong, B. Yao, Z. Xie and L. Wang, *Angew. Chem., Int. Ed.*, 2007, **46**, 1149; (*e*) C. Yang, X. Zhang, H. You, L. Y. Zhu, L. Chen, L. N. Zhu, Y. Tao, D. Ma, Z. Shuai and J. Qin, *Adv. Funct. Mater.*, 2007, **17**, 651.

2 (*a*) K. T. Kamtekar, C. Wang, S. Bettington, A. S. Batsanov, I. F. Perepichka, M. R. Bryce, J. H. Ahn, M. Rabinal and M. C. Petty, *J. Mater. Chem.*, 2006, **16**, 3823; (*b*) S.-J. Su, H. Sasabe, T. Takeda and J. Kido, *Chem. Mater.*, 2008, **20**, 1691; (*c*) Y. Tao, Q. Wang, C. Yang, Q. Wang, Z. Zhang, T. Zou, J. Qin and D. Ma, *Angew. Chem., Int. Ed.*, 2008, **47**, 8104.

3 (*a*) C. Adachi, R. C. Kwong, P. Djurovich, V. Adamovich, M. A. Baldo, M. E. Thompson and S. R. Forrest, *Appl. Phys. Lett.*, 2001, **79**, 2082; (*b*) R. J. Holmes, S. R. Forrest, Y.-J. Tung, R. C. Kwong, J. J. Brown, S. Garon and M. E. Thompson, *Appl. Phys. Lett.*, 2003, **82**, 2422; (*c*) S. Tokito, T. Iijima, Y. Suzuri, H. Kita, T. Tsuzuki and F. Sato, *Appl. Phys. Lett.*, 2003, **83**, 569; (*d*) R. J. Holmes, B. W. D'Andrade, S. R. Forrest, X. Ren, J. Li and M. E. Thompson, *Appl. Phys. Lett.*, 2003, **83**, 3818; (*e*) X. Ren, J. Li, R. J. Holmes, P. I. Djurovich, S. R. Forrest and M. E. Thompson, *Chem. Mater.*, 2004, **16**, 4743; (*f*) S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H. E. Lee, C. Adachi, P. E. Buttows, S. R. Forrest and M. E. Thompson, *J. Am. Chem. Soc.*, 2001, **123**, 4304.

4 (*a*) H. Inomata, K. Goushi, T. Masuko, T. Konno, T. Imai, H. Sasabe, J. J. Brown and C. Adachi, *Chem. Mater.*, 2004, **16**, 1285; (*b*) M.-K. Leung, C.-C. Yang, J.-H. Lee, H.-H. Tsai, C.-F. Lin, C.-Y. Huang, Y. O. Su and C.-F. Chiu, *Org. Lett.*, 2007, **9**, 235.

5 (*a*) S.-J. Yeh, M.-F. Wu, C.-T. Chen, Y.-H. Song, Y. Chi, M.-H. Ho, S.-F. Hsu and C.-H. Chen, *Adv. Mater.*, 2005, **17**, 285; (*b*) M.-H. Tsai, H.-W. Lin, H.-C. Su, T.-H. Ke, C.-C. Wu, F.-C. Fang, Y.-L. Liao, K.-T. Wong and C.-I. Wu, *Adv. Mater.*, 2006, **18**, 1216.

6 J.-J. Lin, W.-S. Liao, H.-J. Huang, F.-I. Wu and C.-H. Cheng, *Adv. Funct. Mater.*, 2008, **18**, 485.

7 T. F. Palmer and S. S. Parmar, *J. Photochem.*, 1985, **31**, 273.

8 (*a*) C. Ego, A. C. Grimsdale, F. Uckert, G. Yu, G. Srdanov and K. Müllen, *Adv. Mater.*, 2002, **14**, 809; (*b*) F. Huang, Y. Zhang, M. S. Liu, Y. J. Cheng and A. K. Y. Jen, *Adv. Funct. Mater.*, 2007, **17**, 3808.

9 P.-I. Shih, C.-H. Chien, F.-I. Wu and C.-F. Shu, *Adv. Funct. Mater.*, 2007, **17**, 3514.

10 Y. Tao, Q. Wang, C. Yang, L. Ao, Q. Wang, J. Qin and D. Ma, *Chem. Commun.*, 2009, 77.

11 K.-T. Wong, Y.-L. Liao, Y.-T. Lin, H.-C. Su and C.-C. Wu, *Org. Lett.*, 2005, **7**, 5131.

12 M. H. Tsai, Y. H. Hong, C. H. Chang, H. C. Su, C. C. Wu, A. Matoliukstyte, J. Simokaitiene, S. Grigalevicius, J. V. Grazulevicius and C. P. Hsu, *Adv. Mater.*, 2007, **19**, 862.

13 (*a*) J. Jacob, S. Sax, M. Gaal, E. J. W. List, A. C. Grimsdale and K. Müllen, *Macromolecules*, 2005, **38**, 9933; (*b*) N. Cocherel, C. Poriel, J. R. Berthelot, F. Barrière, N. Audebrand, A. M. Z. Slawin and L. Vignau, *Chem.–Eur. J.*, 2008, **14**, 11328.

14 E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy and R. N. Adams, *J. Am. Chem. Soc.*, 1966, **88**, 3498.

15 H. You, Y. D. Z. Zhang and D. Ma, *J. Appl. Phys.*, 2007, **101**, 026105.