

Butterfly-Shaped Tetrasubstituted Carbazole Derivatives as a New Class of Hosts for Highly Efficient Solution-Processable Green Phosphorescent Organic Light-Emitting Diodes

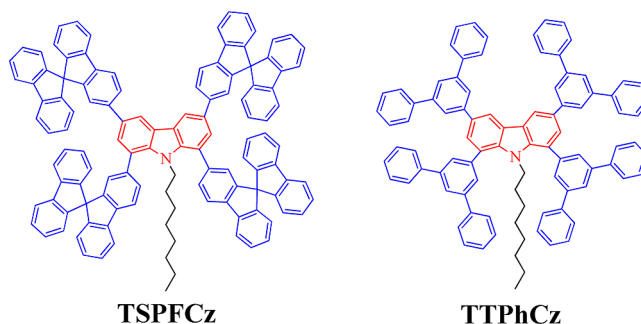
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ABSTRACT



A new bromination method, where butterfly-shaped tetrasubstituted carbazole derivatives TSPFCz and TTPhCz have been designed and synthesized, which possess the twist butterfly skeletons and exhibit excellent thermal and morphological stabilities, has been adopted. By utilizing these novel compounds as host materials, high efficiency solution-processed green phosphorescent organic light-emitting diodes (PhOLEDs) have been achieved.

Phenylamine compounds have been widely applied in organic optoelectronics owing to their rigid structures, excellent hole transporting mobility, and amorphous properties.¹ Among them, carbazole and its derivatives have attracted much attention for application in organic light emitting diodes (OLEDs), photovoltaic cells, and field-effect transistors.² Apart from the general properties of the

phenylamine compounds, carbazole and its derivatives show high triplet energy levels (2.9 eV),³ making them

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(1) Tao, Y.; Yang, C.; Qin, J. *Chem. Soc. Rev.* **2011**, *40*, 2943.

(2) (a) Tsai, M. H.; Hong, Y. H.; Chang, C. H.; Su, H. C.; Wu, C. C.; Matoliukstyte, A.; Simokaitiene, J.; Grigalevicius, S.; Grazulevicius, J. V.; Hsu, C. P. *Adv. Mater.* **2007**, *19*, 862. (b) Ho, C.-L.; Chi, L.-C.; Hung, W.-Y.; Chen, W.-J.; Lin, Y.-C.; Wu, H.; Mondal, E.; Zhou, G.-J.; Wong, K.-T.; Wong, W.-Y. *J. Mater. Chem.* **2012**, *22*, 215. (c) Sujeewa, S.; Palayangoda, X. C.; Adhikari, R. M.; Neckers, D. C. *Org. Lett.* **2008**, *10*, 4. (d) Li, J.; Grimsdale, A. C. *Chem. Soc. Rev.* **2010**, *39*, 2399. (e) Hung, W.-Y.; Chi, L.-C.; Chen, W.-J.; Mondal, E.; Chou, S.-H.; Wong, K.-T.; Chi, Y. *J. Mater. Chem.* **2011**, *21*, 19249. (f) Lai, S. L.; Tong, Q. X.; Chan, M. Y.; Ng, T. W.; Lo, M. F.; Ko, C. C.; Lee, S. T.; Lee, C. S. *Org. Electron.* **2011**, *12*, 541. (g) Ding, J.; Wang, Q.; Zhao, L.; Ma, D.; Wang, L.; Jing, X.; Wang, F. *J. Mater. Chem.* **2010**, *20*, 8126.

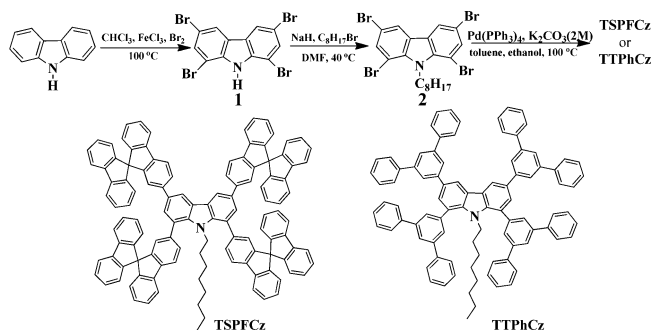
desirable host materials in PhOLEDs. However, their practical applications are usually limited by relatively poor-electron transporting mobility.⁴ In addition, most of the carbazole based small molecules and polymers are constructed by modification at 3,6, 2,7, 1,8 and N linkage positions of carbazole.⁵ For example, Professor Wang synthesized a dendrimer host, by conjugating a moiety to the 3,6 and N positions of carbazole; a fully white PhOLED with a maximum power efficiency of 80.9 lm/W was harvested.⁶ By the modification at the 3,6 and 2,7 positions of the carbazole, some novel compounds were developed and the solution-processed blue PhOLEDs with FIrpic as a dopant showed a low turn-on voltage of 4.0 V, a maximum current efficiency of 27.2 cd/A, a maximum efficiency of 11.8 lm/W, and a maximum external quantum efficiency 14.0%.⁷ Recently, a variety of 1,8-disubstituted carbazole derivatives were reported as fluorescent probes⁸ or to demonstrate the relationship between the rigidity structure and the linking positions.⁹ Generally, the simple structure of a carbazole unit actually offers many choices for introducing building blocks into the system via an easy chemistry approach. However, the tetrasubstituted carbazole derivatives used as the host materials for PhOLEDs have been rarely reported.

In this paper, spirofluorene and benzene units are connected to the 1,3,6,8-positions of the carbazole to form the butterfly-shaped compounds (illustrated in Scheme 1). Compared to the disubstituted carbazole derivatives,¹⁰ the unique butterfly-shaped structure of the molecules enhances the thermal stability of these materials, and the nonplanar linkage modes keep the triplet energy gap at a high level.¹¹ In addition, the long alkyl groups at the N position of the carbazole are beneficial to the solubility of the host materials in the most common solvents. The solution-processed green PhOLEDs with the novel hosts showed excellent performance, with a luminous efficiency ($\eta_{p,max}$) of 41.0 cd/A and an external quantum efficiency ($\eta_{EQE,max}$) of 11.8%. This result is comparative with the recently reported small-molecule host for solution-processed green PhOLEDs.¹²

The butterfly-shaped host materials were realized in three steps with high yields. As shown in Scheme 1, the first step is to prepare the tetrabromocarbazole intermediates.

The second step is to attach the *N*-9-position of the carbazole with a long alkyl group by a simple C–N coupling reaction. The last step involves linking the electron-deficient moiety to the 1,3,6,8-positions of carbazole using a typical Suzuki C–C cross-coupling reaction between the different functional boronic esters and the 1,3,6,8-tetrabromo-*N*-octylcarbazole (**2**). Tetrasubstituted derivatives of carbazole have been rarely reported because it is difficult to obtain tetrabromocarbazole. Only Smith et al.¹³ reported a method of bromination of carbazole by treatment with NBS in the presence of silica gel at ambient temperature. However, the reaction is less selective and gives mixtures of different bromo-substituted derivatives and purification of the tetrabromocarbazole is difficult. Here, we used bromine instead of NBS and used FeCl₃ as the initiator, with the temperature enhanced to 100 °C to promote full substitution in the carbazole. The intermediate 1,3,6,8-tetrabromocarbazole (**1**) can be recrystallized and purified with the solvent ethanol/toluene. Afterwards, 1,3,6,8-tetrabromocarbazole (**1**) was treated with the base NaH, followed by 1-bromooctane, to afford the desired compound **2** in a high yield of 98%. The butterfly-shaped molecules were synthesized by a Suzuki reaction of **2** with 4 equiv of 2-(9,9'-spiro[fluorene]-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane or 2-([1,1':3',1''-terphenyl]-5'-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane with high yields in the range of 75–80% (Scheme 1). All the compounds have been fully characterized by ¹H NMR, ¹³C NMR, mass spectrometry, and elemental analysis (see Supporting Information).

Scheme 1. Synthetic Route for TSPFCz and TTPhCz



The compounds **TSPFCz** and **TTPhCz** exhibited excellent thermal stability with 5% weight-loss decomposition temperatures of 483 and 487 °C, with glass transition temperatures of 236 and 146 °C, respectively, which suggests that they could form morphologically stable and uniform amorphous films. The surface morphologies of thin films of **TSPFCz** and **TTPhCz** were also investigated. The thin film was prepared by spin-coating and then annealed under N₂ gas conditions at 100 °C for 2 h. The annealed film had a fairly smooth surface morphology with a root-mean-square (rms) roughness of 0.45 and 0.38 nm for

(3) Tsai, M. H.; Lin, H. W.; Su, H. C.; Ke, T. H.; Wu, C. c.; Fang, F. C.; Liao, Y. L.; Wong, K. T.; Wu, C. I. *Adv. Mater.* **2006**, *18*, 1216.

(4) Zhang, S. L.; Chen, R. F.; Yin, J.; Liu, F.; Jiang, H. J.; Shi, N. E.; An, Z. F.; Ma, C.; Liu, B.; Huang, W. *Org. Lett.* **2010**, *12*, 3438.

(5) (a) Sasabe, H.; Kido, J. *Chem. Mater.* **2011**, *23*, 621. (b) Park, M. S.; Lee, J. Y. *Chem. Mater.* **2011**, *23*, 4338. (c) Su, S.-J.; Cai, C.; Kido, J. *Chem. Mater.* **2011**, *23*, 274.

(6) Zhang, B.; Tan, G.; Lam, C. S.; Yao, B.; Ho, C. L.; Liu, L.; Xie, Z.; Wong, W. Y.; Ding, J.; Wang, L. *Adv. Mater.* **2012**, *24*, 1873.

(7) Jiang, W.; Duan, L.; Qiao, J.; Dong, G.; Zhang, D.; Wang, L.; Qiu, Y. *J. Mater. Chem.* **2011**, *21*, 4918.

(8) Gee, H. C.; Lee, C. H.; Jeong, Y. H.; Jang, W. D. *Chem. Commun.* **2011**, *47*, 11963.

(9) Wang, H.-Y.; Liu, F.; Xie, L.-H.; Tang, C.; Peng, B.; Huang, W.; Wei, W. *J. Phys. Chem. C* **2011**, *115*, 6961.

(10) Sasabe, H.; Pu, Y. J.; Nakayama, K.; Kido, J. *Chem. Commun.* **2009**, 6655.

(11) Shirota, Y.; Kageyama, H. *Chem. Rev.* **2007**, *107*, 953.

(12) Zhu, M.; Ye, T.; He, X.; Cao, X.; Zhong, C.; Ma, D.; Qin, J.; Yang, C. *J. Mater. Chem.* **2011**, *21*, 9326.

(13) Smith, K.; James, D. M.; Mistry, A. G.; Bye, M. R.; Faulkner, D. J. *Tetrahedron.* **1992**, *48*, 7479.

TSPFCz and **TTPhCz**, respectively (see Figure S2). These demonstrated that the two compounds possess excellent amphotous abilities. The smaller film roughness value of **TTPhCz** compared to **TSPFCz** may be ascribed to the rigid structure of the spirofluorene.

Figure 1 depicts the UV-vis absorption and photoluminescence (PL) spectra of the compounds. The absorption peaks at around 300 nm could be assigned to the $n-\pi^*$ transitions of the carbazole moiety. For the compounds **TSPFCz** and **TTPhCz**, the longer wavelength absorption at around 350 nm could be attributed to $\pi-\pi^*$ transitions from the electron-donating carbazole moiety to spirobifluorene or a 3,5-diphenylbenzene moiety. **TSPFCz** and **TTPhCz** exhibit short emission peaks at 395 and 409 nm, respectively; the red shift of PL of **TSPFCz** compared to **TTPhCz** could be attributed to the larger aromatic conjugation of spirobifluorene. The optical band gaps (E_g) for **TSPFCz** and **TTPhCz** determined from the onsets of their absorption spectra are 3.14 and 3.26 eV, respectively. The triplet energies (E_T) are determined to be 2.52 and 2.73 eV for **TSPFCz** and **TTPhCz**, respectively, by the highest-energy vibronic sub-band of the phosphorescence spectra, which are higher than that of the green emitter of Ir(ppy)₃ ($E_T = 2.42$ eV).

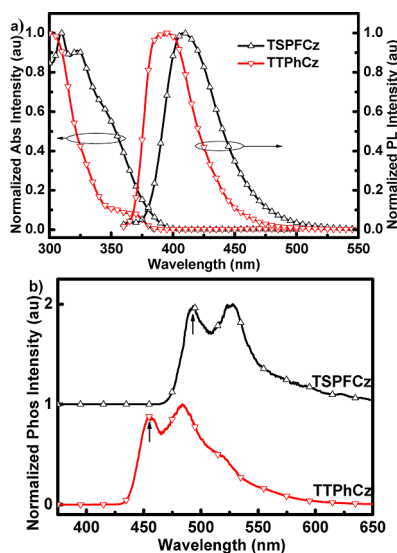


Figure 1. (a) Absorption and emission spectra of **TSPFCz** and **TTPhCz** in toluene solution. (b) Phosphorescent spectra of **TSPFCz** and **TTPhCz** in 2-methyltetrahydrofuran at 77 K.

The electrochemical properties of these compounds **TSPFCz** and **TTPhCz** were investigated by cyclic voltammetry (Figure 2). All of these compounds exhibited a similar quasireversible oxide process with onset potentials of 1.12 and 1.24 eV, respectively. On the basis of the onset potentials for oxidation, the HOMO energy levels of **TSPFCz** and **TTPhCz** were estimated to be -5.52 and -5.54 eV, respectively, with regard to Ag/AgCl (-4.4 eV

below vacuum).¹⁴ The corresponding LUMO levels were calculated from the HOMO values and the energy gaps and were found to be about -2.38 and -2.28 eV, respectively. Density Function Theory (DFT) calculations were performed to understand the physical properties of **TSPFCz** and **TTPhCz** at the molecular level (Figure 3). The HOMO and LUMO levels of **TSPFCz** and **TTPhCz** are mainly located at the electron-donating carbazole and the corresponding fragments, respectively. Especially, **TSPFCz** has almost complete separation of the HOMO and LUMO at the hole and electron transporting moieties; However, **TTPhCz** exhibits only partial separation of the HOMO and LUMO levels, which may be due to the intramolecular charge transfer. The separation between the HOMO and LUMO levels is beneficial to efficient charge-carrier transport and the prevention of reverse energy transfer.¹⁵ The calculated HOMO/LUMO values are in the range of -4.93 to -5.20 / -1.04 to -1.03 eV, which correlate well with the experimental data.

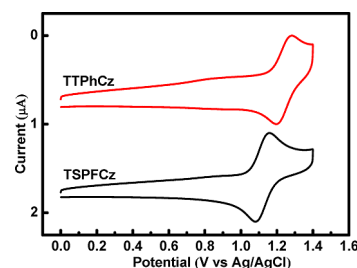


Figure 2. Electrochemical properties of **TSPFCz** and **TTPhCz**.

To evaluate the performance of these compounds as host material, the devices are fabricated by spin-coating with typical structures consisting of multiple organic layers sandwiched between the bottom indium tin oxide (ITO) and the top metal cathode (Al). The device configurations are ITO/PEDOT: PSS (40 nm)/Host: 10 wt % Ir(ppy)₃ (40 nm)/TPBi (40 nm)/LiF (1 nm)/Al. (host: **TSPFCz**, Device A; host: **TTPhCz**, Device B). Polyethylene dioxythiophene-polystyrene sulfate (PEDOT-PSS) and 2,2',2''-(1,3,5-benzenetriyl)tris[1-phenyl-1*H*-benzimidazole] (TPBi) were used as a hole injection and hole-blocking/electron-transporting layer, respectively; Green emitter iridium(III) *fac*-tris(2-phenylpyridine) (Ir(ppy)₃, $E_T = 2.42$ eV) doped in host is used as the emitting layer, with the optimized doping levels of Ir(ppy)₃ at 10%; LiF served as an electron injecting layer.

Current density–voltage–luminance ($J-V-L$) characteristics and the external quantum efficiencies (EQE), current efficiencies (η_c), and electroluminescence spectra (EL) versus current density of the devices are shown in Figure 4. The devices A–B turn on at low voltages in the

(15) (a) Ge, Z.; Hayakawa, T.; Ando, S.; Ueda, M.; Akiike, T.; Miyamoto, H.; Kajita, T.; Kakimoto, M. *Adv. Funct. Mater.* **2008**, *18*, 584. (b) Tao, Y.; Wang, Q.; Yang, C.; Zhong, C.; Zhang, K.; Qin, J.; Ma, D. *Adv. Funct. Mater.* **2010**, *20*, 304.

(14) Sun, Q.; Wang, H.; Yang, C.; Li, Y. *J. Mater. Chem.* **2003**, *13*, 800.

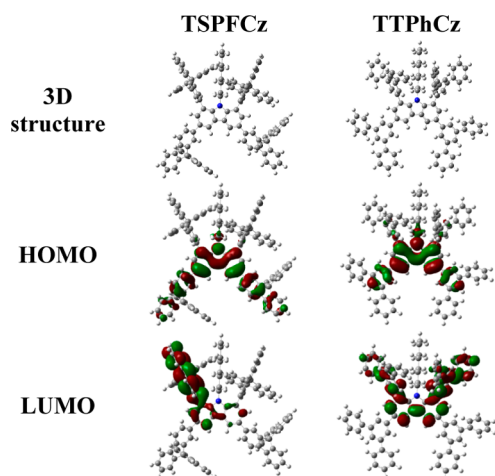


Figure 3. Optimized geometries and calculated HOMO and LUMO density pictures for TSPFCz and TTPhCz.

range 4.0–4.2 V, and device B exhibits a maximum current efficiency and power efficiency (η_p) of 41.0 cd/A and 25.6 lm/W, respectively, and a maximum luminance of 32137 cd/m² at 13.6 V, which is comparable with results recently reported.¹² Values for device A are 36.1 cd/A and 23.1 lm/W, respectively. Devices A–B display typical emission from the green phosphor Ir(ppy)₃ with CIE coordinated (0.30, 0.62) and show slow current-efficiency roll-off (Figure 4b); especially, the maximum current efficiencies for all the devices are acquired at high brightness (~ 100 cd/m²).

All of these results can be attributed to the good thermal stability and the homogeneous film morphology that restrains the strong bimolecular interactions of the phosphorescent Ir(ppy)₃ emitter.¹⁶ To the best of our knowledge, the performance of these devices are among the highest for the solution-processable green phosphorescent OLEDs reported to date.¹⁷

In summary, by adopting a new bromination method, two novel two-dimensional butterfly-shaped tetrasubstituted carbazole derivatives were successfully designed and synthesized. These compounds exhibit excellent thermal and morphological stabilities owing to the rigid tetrasubstituted carbazole skeleton and peripheral aryl groups. Additionally, these novel host materials retain high triplet

(16) Hsu, F.-M.; Chien, C.-H.; Shih, P.-I.; Shu, C.-F. *Chem. Mater.* **2009**, *21*, 1017.

(17) (a) Zhang, M.; Xue, S.; Dong, W.; Wang, Q.; Fei, T.; Gu, C.; Ma, Y. *Chem. Commun.* **2010**, *46*, 3923. (b) Aizawa, N.; Pu, Y.-J.; Sasabe, H.; Kido, J. *Org. Electron.* **2012**, *13*, 2235.

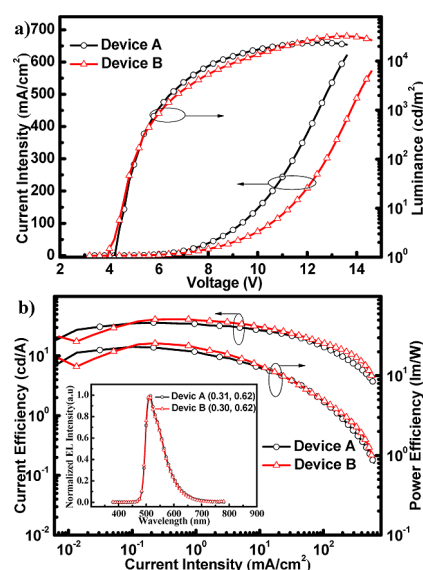


Figure 4. (a) J – V – L characteristics of devices A–B. (b) Current efficiency and power efficiency versus current density of devices A–B; inset: EL spectra of devices A–B.

energy (ca. 2.70 eV) and HOMO levels as carbazole. Solution-processable devices with the novel butterfly-shaped carbazole derivatives as host materials and Ir(ppy)₃ as guest show a maximum current efficiency of 41.0 cd/A and a maximum power efficiency of 25.6 lm/W for green electrophosphorescence. This work reveals the very promising application of butterfly-shaped tetrasubstituted carbazole derivatives as efficient host materials for solution processable PhOLEDs. Further optimization of molecular configuration and device structure is in progress.

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Supporting Information Available. Analytical data and spectra (¹H and ¹³C NMR) for all the products; thermal properties and device performance. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.