ORGANIC
LETTERS

2009
Vol. 11, No. 7
1503−1506

A Fully Diarylmethylene-Bridged Triphenylamine Derivative as Novel Host for Highly Efficient Green Phosphorescent OLEDs

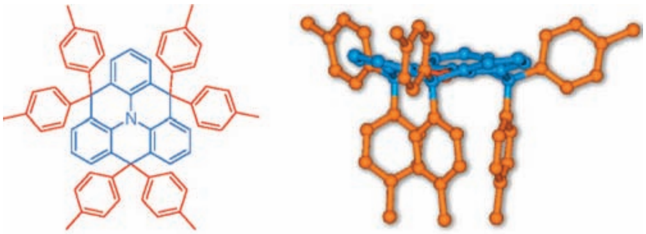
Zuoquan Jiang,[†] Yonghua Chen,[‡] Chuluo Yang,*[,†] Yue Cao,[†] Youtian Tao,[†] Jingui Qin,[†] and Dongge Ma*[,‡]

Department of Chemistry, Hubei Key Laboratory on Organic and Polymeric Optoelectronic Materials, Wuhan University, Wuhan 430072, P. R. China, and State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China

clyang@whu.edu.cn; mdg1014@ciac.jl.cn

Received January 19, 2009

ABSTRACT



A fully diarylmethylene-bridged triphenylamine derivative is efficiently synthesized. It has an almost planar triphenylamine (TPA) skeleton and exhibits excellent thermal and morphological stability. Devices with the novel TPA derivative as host material and Ir(ppy)$_3$ as triplet emitter show a maximum current efficiency of 83.5 cd/A and a maximum power efficiency of 71.4 lm/W for green electrophosphorescence.

Organic light-emitting diodes (OLEDs) based on phosphorescent emitters of heavy metal complexes are currently attracting intensive attention. The strong spin−orbit coupling caused by the heavy metal atom makes the intersystem crossing from the singlet to the triplet states more efficient and, therefore, leads to a 100% internal quantum efficiency in theory.[1] For phosphorescent OLEDs, a host matrix for separation of the triplet emitters is usually required to reduce the concentration quenching and triplet−triplet annihilation.[2] The host for phosphorescent emitters has to fulfill the requirement that the triplet energy of the host has to be higher than that of the guest. This could prevent reverse energy transfer from the guest back to host and confine triplet excitons on guest molecules.[3] It is also desirable that the host has good carrier transport properties for a balanced carrier recombination in the emitting layer.[2c,4] In addition, a bulky and sterically hindered molecular configuration of host is preferable to form morphologically stable and uniform amorphous films.[5]

[†] Wuhan University.

[‡] Changchun Institute of Applied Chemistry.

(1) (a) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Thompson, M. E.; Forrest, S. R. *Nature* **1998**, *395*, 151. (b) Baldo, M. A.; Lamansky, S. P.; Burrows, E.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **1999**, *75*, 4. (c) Adachi, C. M.; Baldo, A.; Thompson, M. E.; Forrest, S. R. *J. Appl. Phys.* **2001**, *90*, 5048. (d) Su, Y.-J.; Huang, H.-L.; Li, C.-L.; Chien, C.-H.; Tao, Y.-T.; Chou, P.-T.; Datta, S.; Liu, R.-S. *Adv. Mater.* **2003**, *15*, 884. (e) Zhou, G.; Wong, W.-Y.; Yao, B.; Xie, Z.; Wang, L. *Angew. Chem., Int. Ed.* **2007**, *46*, 1149. (f) Yang, C.; Zhang, X.; You, H.; Zhu, L. Y.; Chen, L.; Zhu, L. N.; Tao, Y.; Ma, D.; Shuai, Z.; Qin, J. *Adv. Funct. Mater.* **2007**, *17*, 651.

(2) (a) O'Brien, D. F.; Baldo, M. A.; Forrest, S. R.; Thompson, M. E. *Appl. Phys. Lett.* **1999**, *74*, 442. (b) Su, S.-J.; Sasabe, H.; Takeda, T.; Kido, J. *Chem. Mater.* **2008**, *20*, 1691. (c) Tao, Y.; Wang, Q.; Yang, C.; Wang, Q.; Zhang, Z.; Zou, T.; Qin, J.; Ma, D. *Angew. Chem., Int. Ed.* **2008**, *47*, 8104.

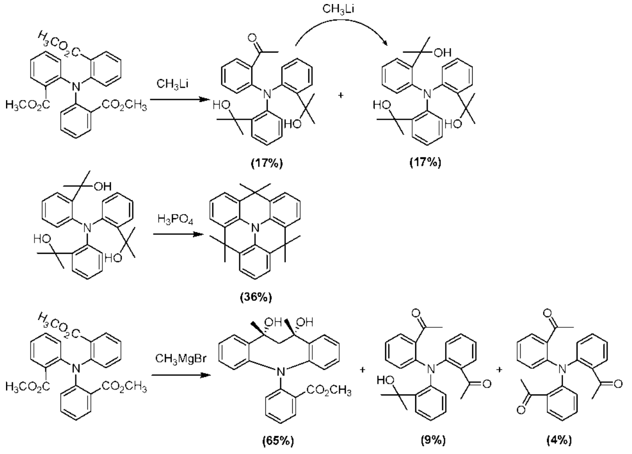
10.1021/ol9001152 CCC: $40.75

As we know, triphenylamine (TPA) has a high triplet energy of 3.04 eV and good hole-transporting ability.[6] These characteristics put the TPA derivatives close to the desired criteria for host material; however, the twisty TPA molecules lack rigidity, which is disadvantageous to the thermal and morphological stabilities of TPA derivatives and consequently hampers their application as host materials in the OLEDs. Thus far, there are very few triphenylamine-based host materials reported. Shu's group reported a high triplet energy host based on TPA/fluorene hybrid for efficient blue (18.1 lm/W, 13.1%) and green (21 lm/W, 12%) electrophosphorescence.[7] We recently reported a TPA/oxadiazole derivative as bipolar host for red elctrophosphorescence (8.2 lm/W, 14.2%).[8]

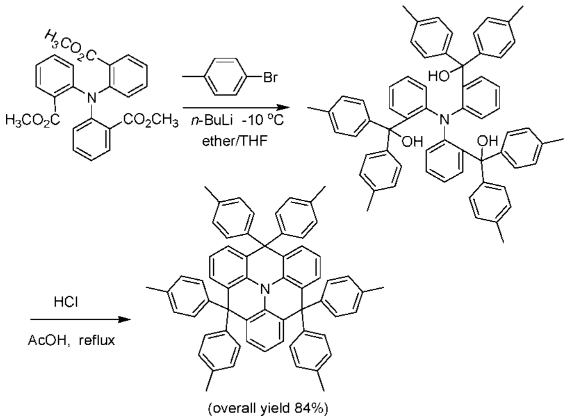
In this paper, we describe the design and synthesis of a fully bridged triphenylamine derivative by using diarylmethylene as the linkage between the *ortho*-positions of the phenyl rings. We anticipate that the rigid TPA skeleton, as well as the peripheral aryl substituents on the bridgehead carbon atom, improve the thermal and morphological stabilities of the triphenylamine derivative without sacrificing the good hole-transport ability and high triplet energy imparted by TPA. In addition, the bulk and sterically hindered molecular configuration is advantageous to effectively separate the triplet emitters.[9]

The bridged TPA derivatives have received little attention. Hellwinkel et al. reported the synthesis of a methylene-bridged TPA by treatment of 2,2′,2″-tricarbomethoxytriphenylamine with methyllithium, and subsequent acid-catalyzed ring closure of the triol with a low yield of ca. 12% in two steps (Scheme 1);[10] most recently, Fang et. al prepared the same compound by using methylmagnesium iodide as nucleophile, and the overall yield is 20%.[11] However, Fox et al. failed to obtain the triol intermediate when using methylmagnesium bromide as nucleophile; instead, they obtained a diol in a yield of 65% (Scheme 1).[12] It is proposed that the methylmagnesium bromide removed the β-H of the acetyl intermediate instead of adding to the carbonyl and thus led to an intramolecular condensation to afford the β-diketone, which was subsequently converted to the diol. Considering the above mechanism, we believe that the use of Grignard or lithium reagent without an α-H, such as aryllithium, could avoid the side reaction in the first step; furthermore, in the ring-closing step, the more stable triphenylmethyl cation could facilitate the Friedel−Crafts reaction. The synthetic route of the target compound is outlined in Scheme 2. The reaction of tricarbomethoxytriphenylamine[13] with an excess amount of 4-methylphenyllithium, generated in situ by treatment 4-bromotoluene with *n*-BuLi at −10 °C, afforded a triol, which subsequently underwent ring closure to give the fully diarylmethylene-bridged TPA (FATPA) in a highly yield of 84% (two steps). The compound was fully characterized by ^{1}H NMR, ^{13}C NMR, mass spectrometry, and elemental analysis (see the Supporting Information).

Scheme 1. Reactions of Tricarbomethoxytriphenylamine with CH_3Li and CH_3MgBr



Scheme 2. Synthesis of FATPA



Colorless crystals of FATPA suitable for X-ray crystallographic analysis were grown by carefully layering a dichloromethane solution of FATPA with ethanol. Its molecular structure is depicted in Figure 1 (the ORTEP drawing is shown in Figure S1, Supporting Information). A torsion angle of 6° between the phenyl ring and basal plane is much smaller than the 35° angle of triphenylamine. The dihedral

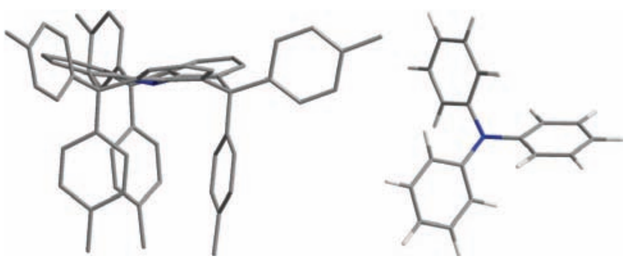


Figure 1. Structural comparison of FATPA (left) and TPA (right).

angle between two phenyl rings linked to the nitrogen is 11° for FATPA, while the angle is 54° for triphenylamine.[14] These parameters indicate that the fully bridged triphenylamine skeleton forms a more planar configuration compared to the twisty triphenylamine structure.

As shown in Figure 1, three *p*-tolyl groups are in axial positions which act as three "desk-legs" to support the "desk plane" (cyclic triphenylamine skeleton), while the other three *p*-tolyl groups are in equatorial positions which splay out around the "desk plane". Such a rigid and sterically bulky molecular configuration is very beneficial for the thermal stability,[15] as indicated by the high thermal decomposition temperatures (T_d, corresponding to 5% weight loss in the thermogravimetric analysis) of 399 °C and a rather high glass-transition temperature (T_g) of 178 °C determined through differential scanning calorimetry (DSC). This value is much higher than those of usual host materials, such as 4,4′-bis(9-carbazolyl)-2,2′-biphenyl (CBP, 62 °C) and 1,3-bis(9-carbazolyl)benzene (*m*CP, 60 °C).[16] As a consequence, the novel compound can form morphologically stable and uniform amorphous films, an essential property for OLEDs upon thermal evaporation.[17]

The electrochemical property of FATPA is studied by cyclic voltammetry, and the compound shows a reversible oxidation process in CH_2Cl_2 solution. The HOMO energy level determined from the onset of the oxidation is 5.22 eV (relative to vacuum energy level), which is almost the same with that of TPA (5.23 eV).[18] This implies that the bridged TPA derivative retains the low hole-injection and good transport ability. The LUMO energy level deduced from the difference between the HOMO level and the optical band gap is 1.62 eV.

Figure 2 shows the room-temperature absorption, fluorescence, and 77 K phosphorescence spectra of FATPA in toluene. FATPA exhibits a electronic absorption at 311 nm and a emission peak at 375 nm. The triplet energy of FATPA was determined to be 2.78 eV by the highest energy vibronic subband of the phosphorescence spectra at 77 K. This value is higher than that of usual host material CBP (2.56 eV), and it may act as appropriate host material for green, red, and even light blue phosphorescent emitters.

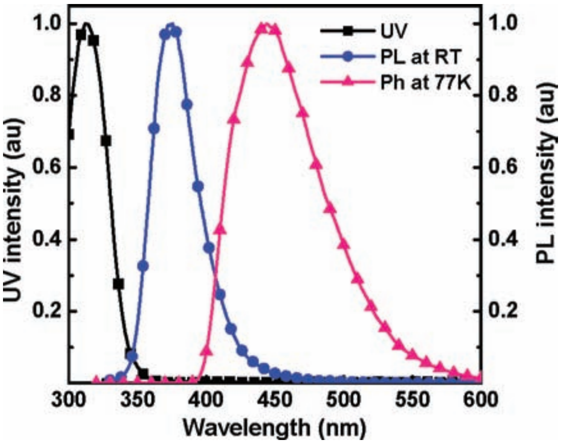


Figure 2. Absorption and emission spectra of FATPA in toluene solution at room temperature and phosphorescence spectrum of FATPA in toluene at 77 K.

To evaluate the performance of FATPA as host material, the devices are fabricated with a typical structures consisting of multiple organic layers sandwiched between the bottom indium tin oxide (ITO) and the top metal cathode (Al). The device configuration is ITO/MoO_3 (10 nm)/NPB (80 nm)/*m*CP (5 nm)/FATPA:Ir(ppy)$_3$ (20 nm)/TAZ (40 nm)/LiF (1 nm)/Al (100 nm). 1,4-Bis[(1-naphthylphenyl)amino]biphenyl (NPB) is used as the hole-transporting material; 1,3-bis(9-carbazolyl)benzene (*m*CP) is used to confine excitons to the emitting layer; 3-(4-biphenylyl)-4-phenyl-5-(4-*tert*-butylphenyl)-1,2,4-triazole (TAZ) is utilized as electron-transporting as well as hole-block material; green-emitter iridium(III) *fac*-tris(2-phenylpyridine) (Ir(ppy)$_3$, $E_T = 2.42$ eV) doped in host FATPA is used as the emitting layer, with optimized doping levels of Ir(ppy)$_3$ at 9%; MoO_3 and LiF serve as hole- and electron-injecting layers, respectively. Current−voltage−luminance (J−V−L) characteristics and current efficiency and power efficiency versus current density of the device are shown in Figure 3. The device turns on at a rather low voltage of 3.3 V. A maximum current efficiency of 83.5 cd/A, equivalent to an external quantum efficiencies 23.4%, is

---

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

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

(5) (a) Inomata, H.; Goushi, K.; Masuko, T.; Konno, T.; Imai, T.; Sasabe, H.; Brown, J. J.; Adachi, C. *Chem. Mater.* **2004**, *16*, 1285. (b) Yang, X.; Müller, D. C.; Neher, D.; Meerholz, K. *Adv. Mater.* **2006**, *18*, 948. (c) Leung, M.-K.; Yang, C-C.; Lee, J.-H.; Tsai, H.-H.; Lin, C.-F.; Huang, C-Y.; Su, Y. O.; Chiu, C.-F. *Org. Lett.* **2007**, *9*, 235.

(6) Palmer, T. F.; Parmar, S. S. *J. Photochem.* **1985**, *31*, 273.

(7) Shih, P.-I.; Chien, C.-H.; Wu, F.-I.; Shu, C.-F. *Adv. Funct. Mater.* **2007**, *17*, 3514.

(8) Tao, Y.; Wang, Q.; Yang, C.; Ao, L.; Wang, Q.; Qin, J.; Ma, D. *Chem. Commun.* **2009**, 77.

(9) Shih, P.-I.; Chiang, C.-L.; Dixit, A. K.; Chen, C.-K.; Yuan, M-C.; Lee, R.-Y.; Chen, C.-T.; Diau, E. W.-G.; Shu, C-F. *Org. Lett.* **2006**, *8*, 2799.

(10) (a) Hellwinkel, D.; Aulmich, G.; Melan, M. *Chem. Ber.* **1974**, *107*, 616. (b) Hellwinkel, D.; Schmidt, W. *Chem. Ber.* **1980**, *113*, 358.

(11) Fang, Z.; Teo, T.-L.; Cai, L.; Lai, Y.-H.; Samoc, A.; Samoc, M. *Org. Lett.* **2009**, *11*, 1.

(12) Fox, J. L.; Chen, C. H.; Luss, H. R. *J. Org. Chem.* **1987**, *52*, 2980.

(13) Field, J. E.; Venkataraman, D. *Chem. Mater.* **2002**, *14*, 962.

(14) Sobolev, A. N.; Belsky, V. K.; Romm, I. P.; Chernikova, N. Yu.; Guryanova, E. N. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *41*, 967.

(15) (a) Wong, K. T.; Chi, L. C.; Huang, S. C.; Liao, Y. L.; Liu, Y. H.; Wang, Y. *Org. Lett.* **2006**, *8*, 5029. (b) Wong, K. T.; Chao, T.-C.; Chi, L. C.; Chu, Y.-Y.; Balaiah, A.; Chiu, S.-F.; Liu, Y-H.; Wang, Y. *Org. Lett.* **2006**, *8*, 5033.

(16) 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.

(17) Kinoshita, M.; Kita, H.; Shirota, Y. *Adv. Funct. Mater.* **2002**, *12*, 780.

(18) This value is evaluated by cyclic voltammetry; see Figure S5 (Supporting Information).

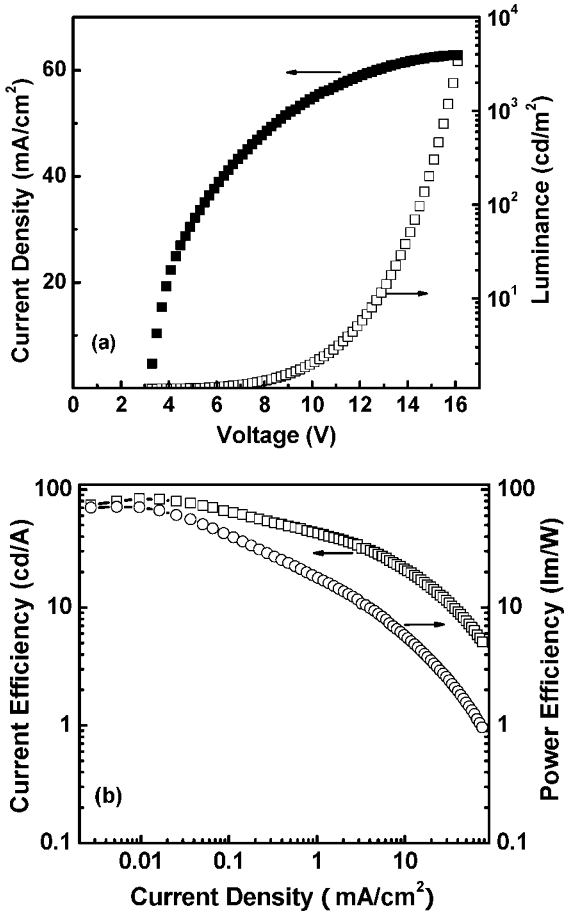


Figure 3. (a) J−V−L characteristics. (b) Current efficiency and power efficiency versus current density of the device.

achieved. High quantum efficiency along with low voltage gives a maximum power efficiency of 71.4 lm/W. These values are much higher than similar CBP- or TAZ-hosted devices[19] and even comparative to those with double emissive layer p−i−n structured devices.[20] To the best of our knowledge, this device performance is among the highest for the green phosphorescent OLEDs reported to date.

In summary, we have developed a convenient and efficient synthesis of fully bridged triphenylamine derivatives. The compound exhibits excellent thermal and morphological stabilities owing to the rigid TPA skeleton and peripheral aryl groups. Moreover, the new host retains high triplet energy (ca. 2.78 eV) and HOMO level as TPA. Devices with the novel TPA derivative as host material and Ir(ppy)$_3$ as guest show a maximum current efficiency of 83.5 cd/A and a maximum power efficiency of 71.4 lm/W for green electrophosphorescence. This work reveals a very promising application of bridged triphenylamine derivatives as efficient host materials. Further optimization of molecular configuration and device structure is in progress.

Acknowledgment. We thank the National Natural Science Foundation of China (Project Nos. 50773057 and 20474047) and the Ministry of Science and Technology of China through the 973 program (Grant No. 2009CB623602) for financial support.

Supporting Information Available: General experimental information; synthesis, characterization, and X-ray structural analysis of FATPA. This material is available free of charge via the Internet at http://pubs.acs.org.

OL9001152

---

(19) (a) Vanslyke, S. A.; Chen, C. H.; Tang, C. W. *Appl. Phys. Lett.* **1996**, *69*, 2160. (b) Adachi, C.; Baldo, M. A.; Forrest, S. R.; Thompson, M. E. *Appl. Phys. Lett.* **2000**, *77*, 904.

(20) He, G.; Pfeiffer, M.; Leo, K.; Pudzich, R.; Salbeck, J. *Appl. Phys. Lett.* **2004**, *85*, 3911.