Diarylmethylene-bridged triphenylamine derivatives encapsulated with fluorene: very high T_g host materials for efficient blue and green phosphorescent OLEDs†

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Two bridged triphenylamine/fluorene hybrids, BTPAF1 and BTPAF2, were designed and synthesized through Friedel–Crafts reaction. Their thermal, electrochemical, electronic absorption and photoluminescent properties were fully investigated. Very high glass transition temperatures (T_g) were observed at 204 °C for BTPAF1 and 211 °C for BTPAF2, owing to the introduction of rigid fluorene and bridged triphenylamine unit. The encapsulation of a fluorene unit at the *para* positions of bridged triphenylamine greatly enhances their electrochemical stability. The linkage by the quaternary carbon atom of the fluorene moiety (C-9) effectively prevents the extension of π-conjugation of the bridged triphenylamine core, and consequently means that the compounds have a high triplet energy of 2.86 eV. Phosphorescent organic light-emitting devices (PHOLEDs) fabricated by using the two compounds as the hosts and the blue emitter bis[2-(4′,6′-difluorophenyl)pyridinato-N,$C^{2'}$]iridium(III) picolate (FIrpic) as the guest exhibit good EL performances with a maximum current efficiency of 20 cd A^{-1}, a maximum power efficiency of 14 lm W^{-1}, and a maximum external quantum efficiency of 9.4%. Green electrophosphorescent devices by using green-emitter iridium(III) *fac*-tris(2-phenylpyridine) [$Ir(ppy)_3$] as guest and the two new compounds as the hosts display excellent EL performances with a maximum current efficiency of 75 cd A^{-1}, a maximum power efficiency of 60 lm W^{-1}, and a maximum external quantum efficiency of 19.5%. The device figures of merit, together with the excellent morphological and electrochemical stabilities, make the new compounds ideal host materials for PHOLEDs, especially for high-temperature applications of devices.

Introduction

Organic light-emitting diodes (OLEDs) have shown promising potential applications in next-generation flat-panel displays and light illumination. Among these devices, tremendous efforts have been made in the development of highly efficient phosphorescent organic light-emitting diodes (PHOLEDs) because they can approach 100% internal quantum efficiency in theory by harvesting both electro-generated singlet and triplet excitons for emission.[1] To fabricate good-performance PHOLEDs, a phosphorescent heavy metal complex as triplet emitter is usually doped into a host matrix to reduce aggregation quenching and triplet–triplet annihilation *etc.*,[2] and thus the choice of host material is of equal importance to triplet dopant. Generally, host material should fulfill the following requirements: (i) higher triplet energy than phosphorescent guest, forbidding energy feedback from the guest to the host; (ii) larger energy gap (E_g) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) than the phosphorescent guest, inducing deep charge trap on dopant emitter;[3] (iii) high glass transition temperature (T_g) to acquire good film morphology, lowering the risk of phase separation upon heating and/or at high loads. However, such requirements become challenged in designing host materials for blue phosphorescent emitter with high triplet energy (E_T > 2.62 eV).[4] Up to now, the major host materials suitable for blue PHOLEDs are based on carbazole derivatives, such as 4,4′-bis(9-carbazolyl)-2,2′-biphenyl (CBP),[1b] 1,3-bis(9-carbazolyl)benzene (*m*CP),[4b] 3,5-bis(9-carbazolyl)tetraphenylsilane (SimCP),[5a] and 9-(4-*tert*-butylphenyl)-3,6-bis(triphenylsilyl)-9*H*-carbazole (CzSi), *etc.*[5b]

Triphenylamine (TPA) is well known for its high triplet energy of 3.04 eV and good hole-transporting ability.[6,7] However, TPA derivatives usually exhibit undesired morphological stabilities due to the nonrigid TPA molecular configuration. In addition, TPA derivatives may polymerize during the device operation due to the existence of an electrochemical active position.[8] The above-mentioned factors hamper the application of triphenylamine derivatives in OLEDs.[9] In the search for new materials capable of hosting blue-emitting phosphors, we have designed two bridged triphenylamine/triphenylsilane hybrids with high triplet energy (2.95 eV).[10] The introduction of triphenylsilane moieties can block the electrochemically active sites and enhance their electrochemical stability. However the bulky

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non-conjugated triphenylsilane groups could be disadvantageous to the charge transporting ability of the compounds. In this article, we report two new diarylmethylene-bridged triphenylamine/fluorene hybrids, BTPAF1 and BTPAF2, by connecting the active *para* positions of the diarylmethylene-bridged triphenylamine with the sp^3-hybridized carbon atom at the C-9 position of the fluorene unit. We choose fluorene to replace triphenylsilane as building block because of its ambipolar carrier transporting properties, high triplet energy (2.95 eV), and high photoluminescent efficiency.[11] Accordingly, we anticipate that the combination of bridged triphenylamine and rigid fluorene unit could impart them with good charge transporting ability, high triplet energy, and high thermal and morphological stabilities, and therefore the hybrids could be efficient hosts for phosphorescent triplet emitters.

Results and discussion

Synthesis and characterization

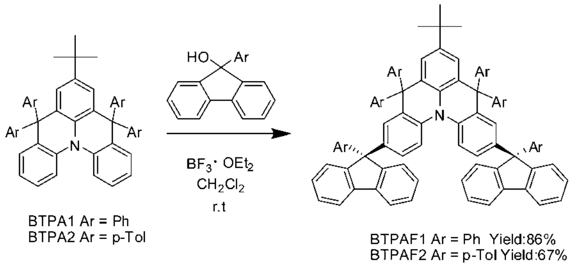
The diarylmethylene-bridged triphenylamine/fluorene hybrids, namely BTPAF1 and BTPAF2, were readily prepared through Friedel–Crafts reaction of diarylmethylene-bridged triphenylamine with 9-aryl-9*H*-fluorenol under the mediation of $BF_3\cdot OEt_2$ in good yields (Scheme 1). The two compounds were fully characterized by ^{1}H NMR, ^{13}C NMR, mass spectrometry and elemental analysis (see Experimental).

Thermal properties

The good thermal stability of the compounds is indicated by the high decomposition temperatures (T_d, corresponding to 5% weight loss) of 491 °C for BTPAF1 and 496 °C for BTPAF2 through thermogravimetric analysis (Fig. 1). Their glass transition temperatures (T_g) appear at 204 °C for BTPAF1 and 211 °C for BTPAF2, in the differential scanning calorimetry (DSC) thermograms (inset of Fig. 1). The T_g values are significantly higher than previous reported triphenylamine/triphenylsilane hybrids (168–173 °C),[10] which should be attributed to the introduction of rigid fluorene unit. As a consequence, the new compounds can form highly thermally durable and morphologically stable thin-film, an essential property for OLEDs upon thermal evaporation.

Photophysical properties

Fig. 2 shows the absorption and photoluminescence spectra of the new compounds. The absorptions in the range of 300–350 nm can be attributed to a π–π* transition of the bridged triphenylamine core, while the absorption around 268 nm can be assigned to a π–π* transition of the fluorene moiety. The characteristic peaks indicate that the linkage by the quaternary carbon atom of the fluorene moiety (C-9) effectively prevents the extension of π-conjugation of the bridged triphenylamine core. The optical band gaps (E_g) determined from the onset of the film absorption spectra are 3.10 eV.



Scheme 1 Synthesis of BTPAF1 and BTPAF2.

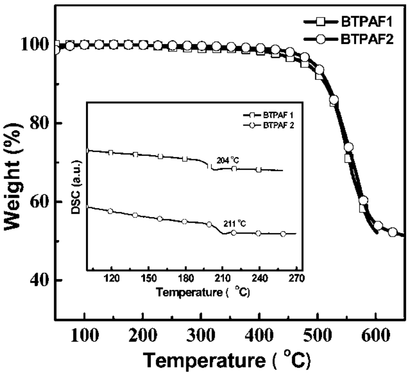


Fig. 1 TGA and DSC (inset) thermograms of BTPAF1 and BTPAF2.

The new compounds exhibit ultraviolet emission at *ca.* 373 nm in the CH_2Cl_2 solution, and 376 nm in film (see ESI, Fig. S1†). The tiny bathochromic shift of film emission with respect to solution reveals that the rigid fluorene moiety as well as the peripheral aryl group on the bridgehead carbon atom can act as effective spacers to suppress the intermolecular aggregation. The inset of Fig. 2 depicts the phosphorescence spectra of the two compounds measured from a frozen toluene matrix at 77 K. Their triplet energies (E_T) are determined to be *ca.* 2.86 eV by the highest energy vibronic sub-band of the phosphorescence spectra. This value is high enough 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). All data are summarized in Table 1.

Electrochemical properties and DFT calculations

The electrochemical behaviors of the new compounds were examined by cyclic voltammetry (CV). They all exhibit a reversible oxidation process. Noticeably, upon repeated scanning, both show reproducible and reversible oxidation behavior (Fig. 3).

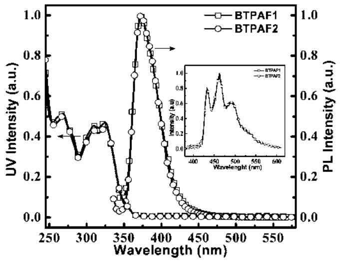


Fig. 2 UV-vis absorption spectra, PL spectra of BTPAF1 and BTPAF2 in CH_2Cl_2 solution, and their phosphorescence spectra in toluene at 77 K (inset).

Table 1 Optical and thermal properties of BTPAF1 and BTPAF2

	BTPAF1	BTPAF2
$T_g/T_m/T_d$(°C)	204/374/491	211/380/496
$\lambda_{abs,\ max}$ (nm) sol[a]/film[b]	325,268/326,269	325,268/328,270
$\lambda_{PL,\ max}$/nm sol[a]/film[b]	374/376	373/376
HOMO[c]/LUMO (eV)[d]	5.19/1.89	5.15/1.85
E_T (eV)[e]	2.86	2.86

[a] Measured in CH_2Cl_2 solution. [b] Measured in film. [c] Determined from the onset of oxidation potentials. [d] Deduced from HOMO and E_g. [e] Triplet energy measured in toluene in 77 K.

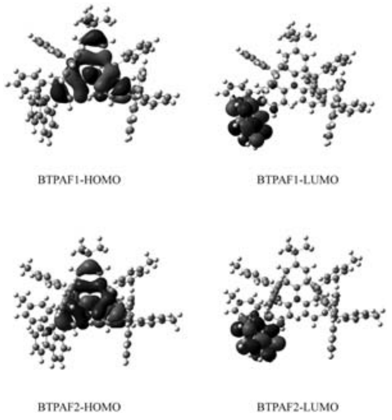


Fig. 4 Spatial distributions of the calculated HOMO and LUMO energy levels of BTPAF1 and BTPAF2.

This contrasts with the irreversible oxidation process of the pristine triphenylamine.[8] Such electrochemical stability can be attributed to the blocking of three active sites of *para*-phenyl positions by *t*-butyl and fluorene moieties, and should benefit the stability of their electroluminescence devices. The HOMO energy levels determined from the onsets of the oxidation potentials are −5.19 eV for BTPAF1 and −5.15 eV for BTPAF2 (relative to vacuum level), respectively, which are higher than that of most widely used NPB (5.4 eV),[12] suggesting no hole-injection barriers from NPB to the compounds.

The geometrical and electronic properties of the compounds were studied by density functional theory (DFT) calculations using the B3LYP hybrid functional. As shown in Fig. 4, the HOMO orbitals of the two molecules are mainly located on the bridged triphenylamine moiety, while their LUMO orbitals are exclusively distributed on the fluorene moiety. The complete separation between HOMO and LUMO levels is favourable to the efficient hole- and electron-transporting properties and the prevention of reverse energy transfer, and thus to benefit to the EL performance of the PHOLEDs.[13]

Phosphorescent OLEDs

To evaluate the performance of the two compounds as host materials for blue and green phosphorescent emitters, we fabricated the devices with the following configurations (Fig. 5): device A–B: ITO/NPB (40 nm)/TCTA (5 nm)/host:FIrpic (20 nm)/TAZ (40 nm)/LiF (1 nm)/Al (100 nm); device C–D: ITO/MoO_3 (10 nm)/NPB (80 nm)/TCTA (5 nm)/host:$Ir(ppy)_3$ (20 nm)/TAZ (40 nm)/LiF (1 nm)/Al (100 nm). In these devices, 1,4-bis(1-naphthylphenylamino)-biphenyl (NPB) was used as the hole-transporting material; 4,4′,4″-tri(*N*-carbazolyl) triphenylamine (TCTA) was used as exciton blocking material; (3-(4-biphenyl-yl)-4-phenyl-5-(4-*tert*-butylphenyl)-1,2,4-triazole (TAZ) was utilized as electron transporting as well as hole blocking material; FIrpic or $Ir(ppy)_3$ doped in host was 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 layer, respectively. The EL spectra of the devices are displayed in Fig. 6. The luminance-current density-current efficiency (L-J-η_c) characteristics of the devices are shown in Fig. 7, and the device data are summarized in Table 2.

The EL spectra show the typical emissions from the blue emitter FIrpic with the Commission Internationale de l'Éclairage (CIE) coordinates of (0.16, 0.32) for devices A and B, and the green emitter $Ir(ppy)_3$ with CIE coordinates of (0.35, 0.62) for devices C and D. The four devices turn on at voltages of 3.5–4.3 V, which are not very low. This may relate to the large electron injection barrier from the electron transporting TAZ layer to the emissive layer. Device A with BTPAF1 as host exhibits a maximum current efficiency of 20 cd A^{-1}, a maximum power efficiency of 14 lm W^{-1}, and a maximum external quantum efficiency of 9.4%, and those data are 19 cd A^{-1}, 14 lm W^{-1}, and 8.9% for device B with BTPAF2 as host. These efficiencies are comparable with or even better than the blue devices using FIrpic as blue emitter under the similar device structures.[14] Both devices C and D reveal highly efficient green electrophosphorescence, with maximum current efficiency, power efficiency and external quantum efficiency of 75 cd A^{-1}, 60 lm W^{-1} and 19.5% for device C, and 78 cd A^{-1}, 54 lm W^{-1} and 18.8% for device D, respectively. These efficiencies are comparable with the best green phosphorescent OLEDs we recently reported.[2c,10] It is noteworthy that all

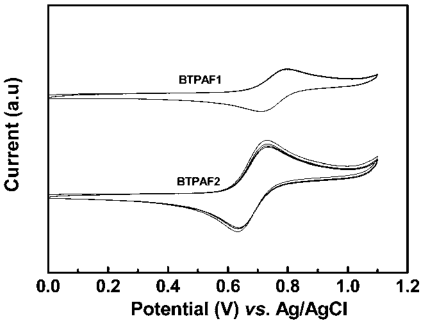


Fig. 3 Cyclic voltammogram of the compounds *vs.* Ag/AgCl.

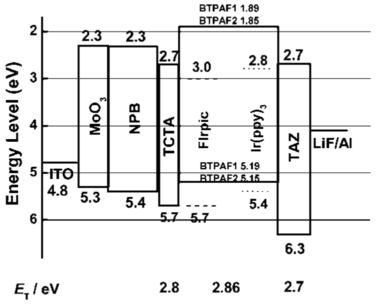


Fig. 5 Device structures and energy level diagram of materials used in the devices.

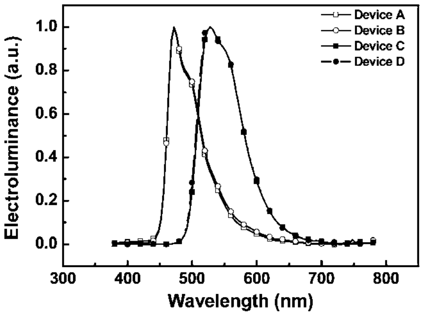


Fig. 6 EL spectra of devices A–D.

Table 2 Summary of device performance

Host	BTPAF1		BTPAF2	
Dopant	FIrpic	Ir(ppy)$_3$	FIrpic	Ir(ppy)$_3$
Device	A	C	B	D
$V_{\text{turn-on}}$/V	4.1	3.7	4.3	3.5
L max/cd m^{-2a}	6988	27 528	10 223	39 411
E.Q.E max (%)^b	9.4	19.5	8.9	18.8
L.E max/cd A^{-1c}	20	75	19	78
P.E max/lm W^{-1d}	14	60	14	54
CIE (x, y)	(0.16, 0.32)	(0.35. 0.62)	(0.17, 0.33)	(0.34, 0.62)

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

the devices display significantly higher luminance than the similar devices using triphenylamine/triphenylsilane hybrids as host materials in our previous report.[10] For example, device B shows a maximum luminance of 10 223 cd m^{-2} at 14 V, which is remarkably enhanced compared to the device hosted by its analogue of triphenylamine/triphenylsilane (1865 cd m^{-2} at 16 V). This could be attributed to the improvement of carrier transporting properties of hosts after the replacement of fluorene for triphenylsilane.

Conclusions

In conclusion, we have designed and synthesized two new host materials for PHOLEDs by the combination of bridged-triphenylamine and fluorene units. The introduction of a fluorene moiety at the *para* positions of bridged triphenylamine greatly improves their thermal and morphological stability, as well as their electrochemical stability. The non-conjugated linkage between the two moieties also ensures the high triplet energies of the hybrids. Devices with the new compounds as host materials show maximum external quantum efficiency as high as 9.4% for blue and 19.5% for green electrophosphorescence. The high device efficiencies could be attributed to the high triplet energy of the host, and complete spatial separation of HOMO and LUMO energy levels. The good device performance, together with the excellent morphological and electrochemical stability, makes the new compounds practical host materials for PHOLEDs.

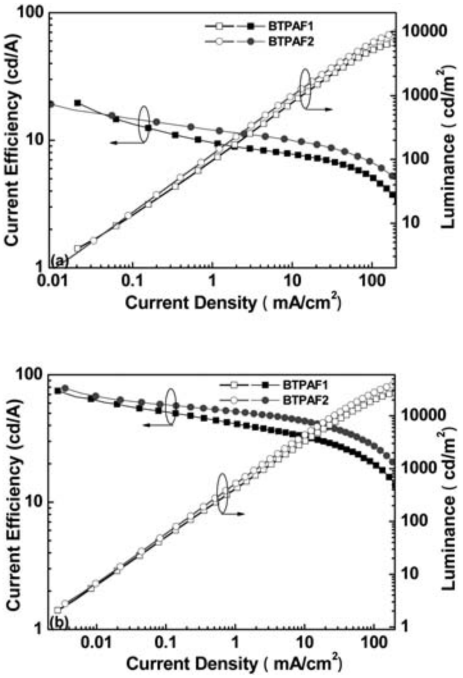


Fig. 7 *L*-*J*-η_c characteristics (a) for the FIrpic-based devices A and B; (b) for the Ir(ppy)$_3$-based devices C and D.

Experimental

General Information

^{1}H NMR and ^{13}C NMR spectra were measured on a Varian Unity 300 MHz spectrometer using CDCl$_3$ as the solvent. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Vario EL-III microanalyzer. MALDI-TOF mass spectrometric measurement was performed on Bruker Biflex III MALDI TOF instrument. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit at a heating rate of 10 °C min^{-1} from 30 to 600 °C under a nitrogen atmosphere. Thermogravimetric analysis (TGA) was undertaken with a NETZSCH STA 449C instrument. The thermal stability of the samples under nitrogen atmosphere was determined by measuring their weight loss, heated at a rate of 10 °C min^{-1} from 25 to 600 °C. UV-Vis absorption spectra were recorded on Shimadzu UV-2550 spectrophotometer. PL spectra were recorded on Hitachi F-4500 fluorescence spectrophotometer. Cyclic voltammetric measurements were carried out on a computer-controlled EG&G Potentiostat/Galvanostat model 283 using tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte in freshly distilled CH$_2$Cl$_2$ solution and conventional three-electrode cell with a Pt work electrode of 2 mm diameter, a platinum-wire counter electrode, and a Ag/AgCl reference electrode.

Preparation of the compounds

7-*t*-Butyl-5,5,9,9-tetraphenyl-13b-aza-naphtho[3,2,1-de]anthracene (BTPA1) and 7-*t*-butyl-5,5,9,9-tetra-*p*-tolyl-13b-aza-naphtho-[3,2,1-de]anthracene (BTPA2) were prepared according to our previous report.[10] All reagents commercially available were used as received unless otherwise stated. The solvents (THF, diethyl ether, dichloromethane) were purified by conventional procedures and distilled under dry argon before using. All reactions were carried out using Schlenk techniques in an argon atmosphere.

Synthesis of BTPAF1. A solution of $BF_3 \cdot OEt_2$ (0.15 ml, 1.2 mmol) in 2 ml of dichloromethane was added dropwise to a solution of 9-phenyl-9*H*-fluoren-9-ol (0.26 g, 1 mmol) and BTPA1 (0.31 g, 0.5 mmol) in 10 ml dichloromethane. The mixture was stirred at room temperature under argon atmosphere for 3 h. Ethanol (5 ml) and water (15 ml) was successively added to quench the reaction. The mixture was extracted with dichloromethane, and then the combined dichloromethane solution was washed with brine and dried over with anhydrous sodium sulfate. After removal of the solvent, the crude product was purified by silicon gel chromatography using 2 : 1 (v : v) petroleum–chloroform as the eluent to afford the product as white solid. Yield: 86%. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.67 (d, J = 7.2 Hz, 4H), 7.27–7.25 (m, 6H), 7.19–7.02 (m, 24H), 6.99–6.81 (m, 16H), 6.74–6.62 (m, 4H), 1.04 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 151.66, 151.46, 146.86, 146.22, 146.06, 140.32, 140.11, 138.92, 137.51, 134.92, 131.87, 131.54, 131.16, 129.31, 128.11, 127.87, 127.71, 127.64, 127.42, 126.45, 126.23, 125.53, 125.35, 120.26, 120.11, 116.51, 65.04, 57.64, 34.48, 31.54. Anal. Calcd. for $C_{86}H_{63}N$ (%): C, 93.02; H, 5.72; N, 1.26. Found: C, 93.00; H, 5.92; N, 1.15. MS (MALDI-TOF) *m/z* 1109.8 [M^+].

BTPAF2. BTPAF2 was synthesized according to the same procedure as BTPAF1 except for using BTPA2 (0.34 g, 0.5 mmol) to replace BTPA1. Yield: 67%. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.66 (d, J = 6.6 Hz, 4H), 7.29–7.24 (m, 6H), 7.14–7.04 (m, 8H), 6.94–6.83 (m, 18H), 6.77–6.66 (m, 12H), 2.32 (s, 6H), 2.24 (s, 6H), 2.23 (s, 6H), 1.07 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 152.00, 151.79, 144.25, 143.38, 143.17, 140.29, 140.01, 138.61, 137.45, 135.82, 135.60, 135.43, 135.00, 131.83, 131.42, 129.18, 128.86, 128.59, 128.01, 127.72, 127.61, 127.28, 127.32, 126.47, 126.18, 125.43, 125.13, 120.24, 120.07, 116.58, 64.71, 56.93, 34.54, 31.67, 21.31, 21.22. Anal. Calcd. for $C_{92}H_{75}N$ (%): C, 92.50; H, 6.33; N, 1.17. Found: C, 92.02; H, 6.40; N, 0.81; MS (MALDI-TOF) *m/z* 1193.9 [M^+].

Device fabrication and measurement

The hole-injection material MoO_3, hole-transporting material NPB (1,4-bis(1-naphthylphenylamino)-biphenyl), exciton blocking material TCTA (4,4′,4′′-tri(*N*-carbazolyl)triphenylamine), hole-blocking and electron-transporting material TAZ (3-(4-biphenyl-yl)-4-phenyl-5-(4-*tert*-butylphenyl)-1,2,4-triazole) were commercially available. Commercial indium tin oxide (ITO) coated glass with sheet resistance of 10Ω/square was used as the starting substrates. Before device fabrication, the ITO glass substrates were pre-cleaned carefully and treated by UV/O_3 for 2 min. Then the sample was transferred to the deposition system. 10 nm of MoO_3 was firstly deposited to ITO substrates, followed by 80 nm NPB, 5 nm TCTA, emissive layer, 40 nm TAZ. Finally, a cathode composed of 1 nm of lithium fluoride and 100 nm of aluminium was sequentially deposited onto the substrates in the vacuum of 10^{-6} Torr to construct the device. The *I*–*V*-B of EL devices was measured with a Keithey 2400 Source meter and a Keithey 2000 Source multimeter equipped with a calibrated silicon photodiode. The EL spectra were measured by JY SPEX CCD3000 spectrometer. All measurements were carried out at room temperature under ambient conditions.

Computational details

The geometrical and electronic properties of the compounds were performed with the Gaussian 03 program package. The calculation was optimized by means of the B3LYP (Becke three parameters hybrid functional with Lee-Yang-Perdew correlation functionals) with the 6-31G(d) atomic basis set 32. Molecular orbitals were visualized using Gaussview.

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