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A host material with a small singlet-triplet exchange energy for phosphorescent organic light-emitting diodes: Guest, host, and exciplex emission

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ABSTRACT

A host material containing a triazine core and three phenylcarbazole arms, called 2,4,6tris(3-(carbazol-9-yl)phenyl)-triazine (TCPZ), was developed for phosphorescent organic light-emitting diodes (OLEDs). Ultra-low driving voltages were achieved by utilizing TCPZ as the host due to its decreased singlet-triplet exchange energy (ΔE_{ST}) and low-lying lowest unoccupied molecular orbital (LUMO) energy level. Interaction between the RGB triplet emitters and TCPZ were studied in both photoluminescent and electroluminescent processes. Transient photoluminescence (PL) measurement of the co-deposited film of fac-tris(2-phenylpyridine) iridium (Ir(PPy)₃):TCPZ exhibits a shoulder at 565 nm whose lifetime is about two times longer than that of the $Ir(PPy)_3$ triplet excitons and can be attributed to the triplet exciplex formed between Ir(PPy)₃ and TCPZ. Such exciplex was also found for the green phosphorescent OLED, giving the most efficient phosphorescent OLED with triplet exciplex emission hitherto. Different from the PL process, a broad featureless band with a maximum at 535 nm was found for the OLED based on an EML of iridium(III) bis(4,6-(di-fluorophenyl)pyridinato-N,C^{2'})picolinate (FIrpic):TCPZ, which can be attributed to the emission from the singlet excited state of TCPZ formed by direct hole-electron recombination. A multi-emitting-layer white OLED was also fabricated by utilizing FIrpic and tris(1-phenylisoquinolinolato- C^2 ,N)iridium(III) (Ir(piq)₃) as the complementary triplet emitters and TCPZ as the host. Different from most of ever reported white OLEDs fabricated with blue/red complementary triplet emitters that exhibit color rendering index (CRI) lower than 70, a high CRI of 82 is achieved due to the combination of blue and red phosphorescence emissions from Flrpic and Ir(piq)₃, and the emerging green fluorescence emission from TCPZ.

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1. Introduction

Since the development on phosphorescent transition metal complexes by Forrest and Thompson's groups, nearly

100% internal quantum efficiency of electroluminescence has been realized by harvesting both electro-generated singlet and triplet excitons by fast intersystem crossing for phosphorescence emission from their triplet states [1]. For those phosphorescent organic light-emitting diodes (OLEDs), phosphorescent emitters are normally doped into an appropriate host material to avoid selfquenching. As thus, it is essential that the triplet energy (E_T) of the host is higher than that of the emitter in order



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to achieve an efficient energy transfer from the host to the guest and also to prevent energy back transfer from the guest to the host [2]. In addition, an optimized carrier recombination in the emitting laver (EML) is also indispensable to give a high efficiency. In general, the electron mobility of many hosts is much lower than the hole mobility because of the fact that they mainly consist of strong electron donors like aromatic amines or carbazoles [3]. Besides the building blocks of electron donors like aromatic amines or carbazoles, introduction of electron deficient heterocycles, like pyridine [4], oxadiazole [5], and phenathroline [6], was proven to be an effective route to give host materials with improved bipolarity. Triazine has an electron affinity larger than those of other typical electron deficient heterocycles (e.g., pyridine, pyrimidine), and its derivatives are known to be good electron transport materials in OLEDs [7]. Besides, some triazine derivatives were also reported as electron-transport type hosts. Adachi and co-workers established a series of 1,3,5-triazine derivatives as hosts for the green phosphor of fac-tris(2-phenylpyridine) iridium (Ir(PPy)₃), resulting in an external quantum efficiency (η_{ext}) of 10.2% and a power efficiency $(\eta_{\rm P})$ of 14 lm W⁻¹ [8]. Wong and co-workers demonstrated a series of 1,3,5-triazine derivatives as hosts for the green phosphors of Ir(PPy)₃ and (PPy)₂Ir(acac), providing maximum η_{ext} and η_{P} of 17.5% and 59.0 lm W⁻¹ [9]. Strohriegl and co-workers demonstrated a series of donor substituted 1,3,5-triazine derivatives as hosts for the blue phosphor of iridium(III) bis(4,6-(di-fluorophenyl)pyridinato-N,C²)picolinate (FIrpic), yielding a maximum current efficiency up to 21 cd A^{-1} [3]. Our previous reports demonstrated that the energy difference (ΔE_{ST}) between the singlet and triplet emission transitions decreases with introducing electron deficient heterocycles combined with electron donors like carbazole, giving host materials as attractive candidates to reduce the driving voltage of OLEDs [10]. It is anticipated that the bipolar host materials consisting of electron acceptor like triazine should also possess a small $\Delta E_{\rm ST}$ to give a reduced driving voltage of OLEDs. However, the introduction of both the electron donor and acceptor to the host material may also lead to an intramolecular charge transfer, resulting in the reduction of the energy band-gap (E_{σ}) of the molecule, and the effect may be much more serious for a triazine-containing bipolar host material because of its higher electron affinity than most of other electron deficient heterocycles. Moreover, as a host material co-deposited with triplet emitters in phosphorescent OLEDs, the interaction between the host material and the triplet emitters and thus the origin of the emitting state are critical factors for the device performance. To date, few works reported on such an interaction, especially for blue, green, and red phosphorescent emitters, which is of importance to realize highly efficient phosphorescent OLEDs for applications to full color flat-panel displays and lighting.

In this article, we report on a bipolar host material composed of 1,3,5-triazine as the core and three phenylcarbazoles as the arms, called 2,4,6-tris(3-(carbazol-9-yl)phenyl)-triazine (TCPZ). Its carrier mobility and energy levels, including the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), singlet and triplet energies, and singlet-triplet exchange energy, were thoroughly characterized. Transient photoluminescence (PL) decays of the co-deposited films with red, green, and blue (RGB) phosphors of tris(1-phenylisoquinolinolato- C^2 , N)iridium(III) (Ir(piq)₃), Ir(PPy)₃, and FIrpic were measured for the study of their interaction in photoluminescence process. In addition, phosphorescent OLEDs were also fabricated with those RGB triplet emitters as the guest and TCPZ as the host for the study of their interaction in electroluminescence process. Moreover, a multiemitting-layer white OLED was fabricated by utilizing FIrpic as a blue emitter and $Ir(piq)_3$ as a complementary red emitter. In contrast to most of ever reported white OLEDs fabricated with blue/red phosphorescent emitters that give CRI lower than 70, a high CRI of 82 is achieved due to the combination of the phosphorescence emissions from $Ir(piq)_3$ and FIrpic and the emerging fluorescence emission from TCPZ.

2. Experimental

2.1. General

All the reagents were purchased from Sigma-Aldrich and were used without further purification. 2,4,6-Tris(3bromophenyl)-triazine (TBrPZ) was synthesized according to the literature procedure [7c]. The developed TCPZ was purified by silica gel chromatography and then repeated thermal gradient vacuum sublimation before characterization and device fabrication. ¹H and ¹³C NMR spectra were recorded on Varian 500 (500 MHz) spectrometer. Mass spectra were obtained using a JEOL JMS-K9 mass spectrometer. Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer Diamond DSC Pyris instrument under nitrogen atmosphere at a heating rate of 10 °C min⁻¹. Thermogravimetric analysis (TGA) was undertaken using a SEIKO EXSTAR 6000 TG/DTA 6200 unit under nitrogen atmosphere at a heating rate of 10 °C min⁻ ¹. UV–Vis absorption spectrum of the neat film was measured with a Shimadzu UV-3150 UV-vis-NIR spectrophotometer. Room temperature steady-state photoluminescent (PL) spectrum of the neat film was obtained with a FluroMax-2 (Jobin-Yvon-Spex) luminescence spectrometer. Ionization potential was determined by atmospheric ultraviolet photoelectron spectroscopy (Rikken Keiki AC-3). Time-resolved emission spectra of the neat film were obtained at T = 4.2 K under excitation by a nitrogen laser $(\lambda = 337 \text{ nm}, 50 \text{ Hz}, 800 \text{ ps})$ combined with a streak scope C4334 (Hamamatsu) and a synchronous delay generator C4792-02) (Hamamatsu). In comparison, transient PL decays and the corresponding simultaneous PL spectra of the phosphorescent emitter-doped films were recorded at room temperature. PL quantum efficiencies of the codeposited films were measured by using an integrating sphere under nitrogen gas flow at room temperature. Density functional theory (DFT) calculations were performed by using the Gaussian suite of programs (Gaussian 03 W). For the calculation of HOMO and LUMO energy levels, the ground state structures were optimized at the restricted B3LYP/6-31G(d) level, and the single-point energies were calculated at the restricted B3LYP/6-311+G(d,p) level. The ground state (S_0) structure optimization and single-point energy calculation were performed at the B3LYP/ 6-31G(d) level. In contrast, the lowest-energy triplet excited state (T_1) structure optimization and single-point energy calculation were performed at the unrestricted B3LYP/6-31G(d) level [11].

2.2. Synthesis of TCPZ

A mixture of TBrPZ (0.979 g, 1.8 mmol), carbazole (1.05 g, 6.3 mmol), PdCl₂ (28.7 mg, 0.162 mmol), tris(tertbutyl)phosphine (131 mg, 0.648 mmol), and sodium tertbutoxide (0.778 g, 8.1 mmol) in anhydrous o-xylene (100 mL) was stirred at 120 °C for 17 h under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into water and then extracted with chloroform. The combined organic phase was washed with brine and dried over MgSO₄. The subjection of the crude mixture to silica gel chromatography (chloroform/n-hexane = 2/1) afforded TCPZ (1.14 g, 79%) as white powders. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.93 (t, J = 2.0 Hz, 3H), 8.74 (d, / = 8.0 Hz, 3H), 8.15 (d, / = 8.0 Hz, 6H), 7.78 (d, J = 8.0 Hz, 3H), 7.73 (t, J = 8.0 Hz, 3H), 7.42 (d, 30.1 Hz)*I* = 8.0 Hz, 6H), 7.33 (t, *I* = 7.0 Hz, 6H), 7.28 (t, *I* = 7.0 Hz, 6H). ¹³C NMR (500 MHz, CDCl₃): δ (ppm) 171.26, 140.76, 138.26, 137.84, 131.30, 130.30, 128.06, 127.60, 126.08, 123.42, 120.32, 120.11, 109.60. MS (EI): m/z 806 [M⁺H⁺] (calcd *m/z* 804.94). Anal. Calc. for C₅₇H₃₆N₆ (%): C, 85.05; H, 4.51; N, 10.44. Found: C, 85.10; H, 4.70; N, 10.14.

2.3. Device fabrication and characterization

Phosphorescent OLEDs were grown on glass substrates precoated with a ~110-nm-thick layer of indium-tin oxide (ITO) having a sheet resistance of 15 Ω/\Box . The substrates were cleaned with ultra-purified water and organic solvents and then dry-cleaned for 20 min by exposure to an UV-ozone ambient. To improve the hole injection from the anode, poly(arylene amine ether sulfone)-containing tetraphenylbenzidine (TPDPES) doped with 10% (by weight) tris(4-bromophenyl) aminium hexachloroantimonate (TBPAH) was spun onto the precleaned substrate from its dichloroethane solution to form a 20-nm-thick polymer buffer layer [12]. For the red phosphorescent OLEDs, a 35nm-thick 1,1-bis(4-(N,N-di(p-tolyl)-amino)phenyl)cyclohexane (TAPC) was deposited onto the buffer layer as a hole-transport layer (HTL). Then, 4% (by weight) Ir(piq)₃ was co-deposited with TCPZ to form a 10-nm-thick EML. Finally, a 65-nm-thick electron-transport layer (ETL) of 2,4,6-tris(3'(pyridin-2-yl)biphenyl-3-yl)-1,3,5-triazine (TmPyBPZ) [7c] was deposited to block holes and to confine excitons in the emissive zone. For the green phosphorescent OLEDs, TAPC (30 nm), Ir(PPy)₃ (8 wt.%):TCPZ (10 nm), and TmPyBPZ (50 nm) were successively deposited as the HTL, EML, and ETL, respectively. 2,2'-Bis(m-dip-tolylaminophenyl)-1,1'-biphenyl (3DTAPBP) (30 nm), FIrpic (11 wt.%):TCPZ (10 nm), and 3,5,3',5'-tetra(*m*-pyrid-3-yl)phenyl-(1,1')-biphenyl (BP4mPy) [13] (40 nm) were successively deposited as the HTL, EML, and ETL, respectively, for the blue phosphorescent OLEDs. For the white OLEDs, TAPC (30 nm) and 1,3-bis(3,5-dipyrid-3-yl-phenyl) benzene (BmPyPB) [14] (40 nm) were deposited as the HTL and ETL, respectively. A multi-emitting-layer comprising TCPZ:FIrpic (11 wt.%) (4.75 nm), TCPZ:Ir(piq)₃ (4 wt.%) (0.5 nm), and TCPZ:FIrpic (11 wt.%) (4.75 nm) were successively deposited between the HTL and ETL. Cathodes consisting of a 0.5-nm-thick layer of LiF followed by a 100-nm-thick layer of Al were patterned using a shadow mask with an array of 2×2 mm openings. The electroluminescent (EL) spectra were recorded by an optical multi-channel analyzer, Hamamatsu PMA 11. The current density and luminance versus driving voltage characteristics were measured by Keithley source-measure unit 2400 and Konica Minolta chroma meter CS-200, respectively. η_{ext} is calculated from the luminance, current density, and EL spectra, assuming a Lambertian distribution.

For the carrier mobility measurement, the neat film of TCPZ (~1.6 µm) was prepared on the ITO-coated substrates. A semi-transparent Al layer was patterned using a shadow mask with an array of 2 × 2 mm openings. The hole/electron mobility was measured by using a conventional photo-induced time-of-flight (TOF) technique. A nitrogen laser was used as the excitation source (λ = 337 nm) and was incident on the sample through the ITO or semi-transparent Al electrode.

3. Results and discussion

As shown in Scheme 1, TCPZ was synthesized by a Palladium catalyzed amination reaction between TBrPZ and carbazole. UV-vis absorption and steady-state PL spectra of the vacuum-deposited film (60 nm) of TCPZ on guartz substrate were measured at room temperature (Fig. 1a). The absorption peaks and shoulders at 283, 296, 329, and 343 nm can be attributed to the π - π ^{*} transitions of the carbazole chromophore of TCPZ. The absorption peaks at 244 and 267 nm can be attributed to the $n-\pi^*$ and $\pi-\pi^*$ transitions of the central 2,4,6-triphenyl-1,3,5-triazine skeleton, respectively. Different from the previously reported carbazole substituted 1,3,5-triazine derivatives where the carbazole is directly combined with the triazine through its 9-position (λ_{abs} = 289 and 333 nm) [3,8], there is a little bathochromic shift in absorption peaks of carbazole, and it can be attributed to the insertion of phenyl between the triazine core and the carbazole periphery that induces an elongated π conjugation although they are combined with each other at the meta positions. In addition, another pronounced phenomenon is that absorption at wave-



Scheme 1. Synthetic route of TCPZ. (i) CF₃SO₃H, anhydrous chloroform, 0–25 °C; (ii) PdCl₂, tris(*tert*-butyl)phosphine, sodium *tert*-butoxide, anhydrous *o*-xylene, 120 °C.



Fig. 1. (a) Room temperature UV/vis absorption and steady-state photoluminescence spectra for the vacuum-deposited neat film of TCPZ on quartz substrate. (b) Time-resolved emission spectra for the vacuumdeposited neat film of TCPZ excited by a nitrogen laser ($\lambda = 337$ nm, 50 Hz, 800 ps) at T = 4.2 K. Black line: emission spectrum of the prompt component (0.23 ms < t < 0.60 ms), mostly composed of fluorescence. Grey line: emission spectrum of the delayed component (1 ms < t <10 ms), also called phosphorescence.

lengths longer than 350 nm emerges in contrast to the other donor substituted triazines. It can be attributed to the strong electron affinity of triazine and intramolecular charge transfer between the central triazine and the outer carbazole through the phenyl bridges. From the absorption edge, E_g of TCPZ can be assumed to be 2.95 eV, which is much narrower than that of the analogues without any phenyl bridges (E_g = 3.4 eV) [3,8]. Similar to the absorption spectrum, PL spectrum of TCPZ is also shifted to the longer wavelength in comparison with the analogues without any phenyl bridges (λ_{PL} = 392 nm) to give a featureless emission peak at 467 nm. It also shows a larger Stokes shift compared with the analogues without any phenyl bridges, further indicating that the origin of the emission from TCPZ is based on the intramolecular charge transfer between the central triazine and the outer carbazole.

To obtain $E_{\rm T}$ of TCPZ, extremely long decay components of its transient photoluminescence lasting for ~ 10 ms were recorded at T = 4.2 K. Fig. 1(b) shows two time-resolved emission spectra. One is the emission spectrum of the prompt component (0.23 ms < t < 0.60 ms), mostly composed of singlet emissions, also called fluorescence spectrum, which is almost consistent with the steady-state PL spectrum that measured at room temperature. From the highest energy fluorescence peak $S_0^{\nu=0} \leftarrow S_1^{\nu=0}$, singlet energy (E_S) of TCPZ can be estimated as 2.66 eV. The other is the emission spectrum of the delayed component (1 ms < t < 10 ms), generally consisting of only triplet emissions, also called phosphorescence spectrum. TCPZ exhibits the highest energy phosphorescence peak $S_0^{\nu=0} \leftarrow T_1^{\nu=0}$ at 492 nm, corresponding to $E_{\rm T}$ of 2.52 eV. Generally, a favorable exchange energy as small as possible is requested for a host material to allow for both charge injection into the host and efficient triplet emission from a dispersed triplet emitter. Here, the energy difference between the singlet and triplet emission transitions is taken as an estimate for the exchange energy, and ΔE_{ST} of TCPZ was estimated

to be 0.14 eV. In contrast, $\Delta E_{\rm ST}$ of the analogues without any phenyl bridges is 0.35 eV, which is much larger than that of TCPZ. Moreover, $\Delta E_{\rm ST}$ of TCPZ is also much smaller than those of the previously reported host materials [10,15], indicating that TCPZ may be an attractive candidate for the host of phosphorescent OLEDs giving reduced driving voltages. Most recently, a triazine derivative of 2biphenyl-4,6-bis(12-phenylindolo[2,3-a]carbazole-11-yl)-1,3,5-triazine was reported with a $\Delta E_{\rm ST}$ of 0.11 eV [16]. However, it was used as an emitting dopant to achieve an efficient singlet emission, and the effect of $\Delta E_{\rm ST}$ on the driving voltage of the device was not demonstrated.

HOMO energy level of TCPZ determined by atmospheric photoelectron spectroscopy is 6.18 eV. Its LUMO energy level estimated from the HOMO energy level and E_g is 3.23 eV. Compared with a general host material of *N*,*N*⁻ dicarbazolyl-4,4'-biphenyl (CBP) without any electron deficient heterocycle (LUMO = 2.7 eV) [15], much lower-lying LUMO energy level is achieved by introducing triazine with high electron affinity as the core. Its LUMO energy level is also much lower-lying than that of the analogues without any phenyl bridges (LUMO = 2.6 eV) due to the reduced E_g [8], indicating a relatively lower electron-injection barrier from the electron-transport layer.

In addition, TCPZ shows a glass transition temperature (T_g) as high as 162 °C and a melting temperature (T_m) of 323 °C. In comparison, CBP shows a crystalline behavior, and no T_g was detected in its DSC thermogram [17]. No T_g was also found for the carbazole substituted triazine derivatives without any phenyl bridges [3,8]. The high T_g of TCPZ proves the high morphologic stability of the amorphous phase in a deposited film, which is a prerequisite for its applications in OLEDs.

DFT calculations were performed using the Gaussian suite of programs (Gaussian 03 W) for the structure of TCPZ. As shown in Fig. 2, HOMO of TCPZ is mainly located at the outer carbazoles. In contrast, its LUMO is mainly located at the central 2,4,6-triphenyl-1,3,5-triazine skeleton among the outer carbazoles, giving a low-lying LUMO energy level due to the strong electron affinity of triazine. In addition, the calculated spatial distributions show limited overlap between its HOMO and LUMO, further indicating localized HOMO and LUMO energy levels on the carbazole and triphenyltriazine, respectively.

Its triplet energy is also calculated by the difference of their ground state (S_0) and triplet excited state (T_1) energies, and the calculated triplet energy $(T_1 - S_0)$ of TCPZ is 2.72 eV. The energy difference (ΔE) between E_g and $(T_1 - S_0)$ is taken as an estimate for the energy difference between the singlet and triplet transitions, and ΔE of 0.39 eV is obtained for TCPZ. Our previously demonstrated bipolar host materials containing a pyridine core have ΔE of 0.83-1.06 eV, and the bipolar host materials with a pyrimidine core have ΔE of 0.53–0.57 eV [10]. Since the electron affinity of triazine is stronger than that of pyridine and pyrimidine, a reduced ΔE seems to be achieved for the bipolar host materials by introducing a heterocycle with stronger electron affinity. This is also proved by the experimental result that ΔE_{ST} of TCPZ is much smaller than those of the host materials containing heterocycles like pyridine and pyrimidine [10].



HOMO = 5.77 eV

LUMO = 2.66 eV

Fig. 2. The calculated spatial distributions and energy levels of HOMO and LUMO for TCPZ.

As former mentioned, as a host material for a triplet emitter, its triplet excited state should be higher than that of the triplet emitter to prevent reverse energy transfer from the guest to the host. Compared with the bipolar host material containing a pyridine or pyrimidine core, decreased E_T is obtained for TCPZ. It seems in contradiction with this requirement. To verify its triplet exciton confinement ability, well-known red, green, and blue triplet emitters of Ir(piq)₃, Ir(PPy)₃, and FIrpic were co-deposited with TCPZ for transient PL decay measurements.

Since $E_{\rm T}$ of TCPZ is slightly lower than that of FIrpic (2.61 eV), it is anticipated that there should be a back energy transfer from FIrpic to TCPZ. As shown in Fig. 3, FIrpic (3 wt.%) doped into TCPZ exhibits a complex decay curve, which can be well-fitted with a third exponential decay curve to give a short first exponential component lifetime of 0.45 µs. In addition, its PL quantum efficiency ($\eta_{\rm PL}$) is (66 ± 1)%. The complex decay curve and the relatively low $\eta_{\rm PL}$ can be attributed to lower $E_{\rm T}$ of TCPZ than FIrpic and thus reverse energy transfer from FIrpic to TCPZ and

thus a non-radiative deactivation. The simultaneous PL spectrum features emission bands at 475 and 510 nm, which are identical to the PL bands of FIrpic (Fig. 4), indicating all the emissions originate from the triplet excited state of FIrpic.

For the co-deposited film of $Ir(PPy)_3$ (8 wt.%):TCPZ, it also shows a complex decay curve with a short first exponential component lifetime of 0.56 µs and a relatively low η_{PL} of (69 ± 1) %. It is of interest that its PL spectrum is slightly different from that of $Ir(PPy)_3$ with improved shoulder at 560 nm (Fig. 4), and the PL spectrum in the whole range (0 < *t* < 20 µs) can be divided into that from $Ir(PPy)_3$ and another new band with a maximum peak at 565 nm and a shoulder at 530 nm (Fig. 4, grey lines), and the emission components from $Ir(PPy)_3$ and the new band are quite similar. To study the origin of this new band, the emissions in the range of 1.5–2.5 µs (Fig. 5c – c2) and 10– 20 µs (Fig. 5c – c3) were recorded in combination of the emissions in the whole range (0<*t*<20 µs) (Fig. 5c – c1), as indicated in Fig. 5(a). It can be clearly seen that the



Fig. 3. Black solid lines: transient photoluminescence decay curves for the red (Ir(piq)₃, 4 wt.%), green (Ir(PPy)₃, 8 wt.%), and blue (FIrpic, 3 wt.%) triplet emitters co-deposited with TCPZ. Grey dotted lines: the exponentially fitted decay curves for the corresponding films.



Fig. 4. Photoluminescence spectra for the triplet emitters (FIrpic (3 wt.%), $Ir(PPy)_3$ (8 wt.%), and $Ir(piq)_3$ (4 wt.%)) co-deposited with TCPZ. The photoluminescence spectrum of TCPZ: $Ir(PPy)_3$ is divided into the emission bands from $Ir(PPy)_3$ and the triplet exciplex (Grey lines).

emission spectrum in the range of 1.5-2.5 µs is almost identical to that of Ir(PPy)₃, and the emission spectrum in the range of $10-20 \,\mu s$ is guite similar to the new band that shown in Fig. 4. Their different lifetimes and emission spectra suggest that the emitting state of the new band is not the Ir(PPy)₃ triplet excited state. Due to its relatively longer lifetime, the new band can be assumed to be originated from the triplet exciplex formed between TCPZ and Ir(PPy)₃. Although emissions from Ir(PPy)₃ and the triplet exciplex are covered with each other between 500 and 650 nm, most of emissions at the wavelengths shorter than 500 nm should be originated from the relaxation of Ir(P-Py)₃ triplet excited state, and most of emissions at the wavelengths longer than 650 nm should be originated from the triplet exciplex. Their corresponding decay curves are shown in Fig. 5(b) as b2 and b3, respectively, in comparison with that of the emissions in the range of 400-700 nm b1, as indicated in Fig. 5(a). It can be clearly seen that the lifetime of b2 is much lower than that of b3. The transient decays of b2 and b3 were well-fitted by:

$$I_{\rm PL}(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \tag{1}$$

h2

and the transient decay of b1 was well-fitted by:

$$I_{\rm PL}(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3}$$
⁽²⁾

where I_{PL} is the photoluminescence intensity, A_1 , A_2 , and A_3 are quantities of the corresponding emission components, t is decay time, and τ_1 , τ_2 , and τ_3 are the lifetimes of the corresponding emission components. As shown in Table 1, the first exponential component lifetime (τ_1) is 0.65 µs for b2, which is about half of that for b3. Although the emissions in the range of 400–700 nm are comprised of emissions from Ir(PPy)₃ and the triplet exciplex, it shows a short τ_1 of 0.56 µs, which is quite similar to that for b2, indicating its first exponential component is mainly originated from the triplet excited state of $Ir(PPy)_3$. This further proves that the emission lasting for a short time is identical to that of Ir(PPy)₃. In addition, it also shows τ_2 of 1.82 µs, which is slightly longer than τ_1 for b3, indicating the second exponential component is most likely originated from the triplet exciplex. Moreover, the quantities of the emission components (A_1 and A_2 for b1) are similar to each other, further proving that the emission components from Ir(PPy)₃ and the triplet exciplex are similar. The elongated



-h3

Fig. 5. (a) Image of transient photoluminescence decay for the co-deposited film of TCPZ:Ir(PPy)₃ (8 wt.%). (b) Transient photoluminescence decay curves according to the emissions in the range of 400–700 nm (b1), 400–500 nm (b2), and 650–700 nm (b3), as indicated in (a). (c) The emission spectra in the range of 0–20 μ s (c1), 1.5–2.5 μ s (c2), and 10–20 μ s (c3), as indicated in (a). (d) Scheme of the singlet and triplet energy levels for TCPZ and Ir(PPy)₃ and the triplet exciplex formed between triplet excited states of TCPZ and Ir(PPy)₃.

Table 1

Exponentially fitted lifetimes (τ_1 , τ_2 , and τ_3) and quantities (A_1 , A_2 , and A_3) of the corresponding emission components for the transient photoluminescence decay of the co-deposited films of TCPZ:FIrpic (3 wt.%), TCPZ:Ir(PPy)₃ (8 wt.%), and TCPZ:Ir(piq)₃ (4 wt.%).

Guest	$\eta_{ m PL}$ (%)		Wavelength (nm)	τ_1 (µs)	A_1	τ ₁ (μs)	<i>A</i> ₂	τ ₃ (μs)	A ₃
FIrpic	66 ± 1		350-650	0.45	0.50	1.92	0.49	6.58	0.10
Ir(PPy) ₃	69 ± 1	b1 b2 b3	400–700 400–500 650–700	0.56 0.65 1.29	0.54 5.78 1.43	1.82 3.50 4.74	0.44 0.19 0.49	5.90 - -	0.10 - -
Ir(piq) ₃	54 ± 1		520-820	1.15	1.10	-	-	-	-

lifetime for b3 indicates the new emission band should arise from the triplet exciplex formed between the triplet excited states of TCPZ and Ir(PPy)₃. After the formation of the TCPZ and Ir(PPy)₃ triplet excited states, there should be a charge transfer in the Ir(PPy)₃:TCPZ exciplex, giving an elongated lifetime (Fig. 5d). As shown in Fig. 6, the emission intensity at longer wavelengths increases with the increment of Ir(PPy)₃ concentration, further proving that the emission at longer wavelengths originates from the Ir(PPy)₃:TCPZ triplet exciplex. Note that an exciplex is an excited state whose wave function straddles two dissimilar molecules, one a net electron donor and the other an acceptor, and strong spin-orbital coupling of Ir presumably leads to the formation of a triplet exciplex [18]. In this system, TCPZ more likely behave as an electron acceptor due to the strong electron affinity of its triazine core.

For Ir(piq)₃ with the lowest triplet energy among these phosphorescent emitters, the co-deposited film of Ir(piq)₃ (4 wt.%):TCPZ exhibits a clear mono-exponential decay curve with relatively long lifetime of about 1.15 µs and radiative and nonradiative rate constants (k_r and k_{nr}) of 4.7 × 10⁵ and 4.0 × 10⁵ s⁻¹, respectively. Its η_{PL} is (54 ± 1)%, which is one of the highest values for the Ir(piq)₃-doped films. The simultaneous PL spectrum features emission bands at 627 and 683 nm, which are identical to the photoluminescent bands of Ir(piq)₃ (Fig. 4), indicating all the emissions originate from the triplet excited state of Ir(piq)₃. The transient PL observation indicates that the triplet energy transfer from Ir(piq)₃ to TCPZ is completely suppressed and the



Fig. 6. Photoluminescence spectra for the co-deposited films of TCPZ: $Ir(PPy)_3$ at different $Ir(PPy)_3$ concentrations.

energy is well-confined on the $Ir(piq)_3$ molecules due to its higher E_T than the guest.

Since the charge carriers are recombined in the EML in an OLED, balanced carrier injection and transport into the EML is a prerequisite for improved device performance. As thus, different from the hole-transport and electrontransport materials, balanced hole and electron mobility is ideal for a host material. Hole/electron mobility of TCPZ was measured by using a conventional photo-induced TOF technique using a nitrogen laser as an excitation source $(\lambda = 337 \text{ nm})$. Fig. 7 shows its hole $(\mu_{\rm h})$ and electron $(\mu_{\rm e})$ mobility plotted as a function of the square root of the electric field (*E*). $\mu_{\rm h}$ of TCPZ lies in the range from 3.8 \times 10^{-5} to 4.6×10^{-5} cm² V⁻¹ s⁻¹ at electric field between 8.1×10^5 and 1.0×10^6 V cm⁻¹, which is quite similar to its μ_{e} , ranging from 2.7×10^{-5} to 5.4×10^{-5} cm² V⁻¹ s⁻¹ at electric field between 6.4×10^5 and $1.0 \times 10^6 \, V \, cm^{-1}$. Different from many carbazole-based host materials that exhibit higher $\mu_{\rm h}$ than $\mu_{\rm e}$ due to the well-known electron donor carbazole moiety, the similarity of μ_h and μ_e suggests that TCPZ behaves more like a bipolar host material, further proving the validity of the molecular design [10].

To valuate TCPZ as a host material for phosphorescent emitters, OLEDs were fabricated by doping $Ir(piq)_3$, $Ir(PPy)_3$, and FIrpic into TCPZ as the EMLs, respectively. The $Ir(piq)_3$ -based red phosphorescent OLED shows a turn-on voltage (V_{on}) of 2.3 V for electroluminescence (luminance of 1 cd m⁻² was detected) and driving voltages



Fig. 7. Hole (μ_h) (open circles) and electron (μ_e) (closed circles) mobility for the neat film of TCPZ plotted as a function of the square root of the electric field (*E*). *Inset*: typical transient photocurrent signals for electron and hole.

of 3.02 and 4.25 V achieved at 100 and 1000 cd m^{-2} , respectively (Fig. 8), which are the lowest driving voltages hitherto [10] and are even lower than those of the devices based on a *p-i-n* architecture [19]. The low driving voltages achieved here can be attributed to the low-lying LUMO energy level and the small $\Delta E_{\rm ST}$ of TCPZ, giving an improved carrier injection into the EML. Note that the concentration of Ir(piq)₃ is as low as 4 wt.%. At low current density, carriers may be injected into the EML through the Ir(piq)₃ dopant molecules because of its lower-lying LUMO (3.4 eV) and higher-lying HOMO (5.4 eV) energy levels. But at high current density, more carriers must be injected into the EML through the host molecules. The reduced driving voltage achieved by utilizing TCPZ proves that more carriers must be injected into the EML through the host rather than direct carrier trap by the dopant. Aside from the low driving voltage, a very high maximum η_{ext} of 19.1% and a maximum $\eta_{\rm P}$ of 20.5 lm W⁻¹ were achieved at low current density. The efficiencies are 17.9%, 15.8 lm W^{-1} and 14.1%, 8.85 lm W^{-1} at 100 and 1000 cd m⁻², respectively, which is one of the highest efficiencies for the $Ir(piq)_{3}$ -



Fig. 8. (a) Current density (open) and luminance (closed) vs driving voltage and (b) external quantum efficiency (η_{ext}) (closed) and power efficiency (η_P) (open) vs luminance characteristics of the phosphorescent OLEDs in structures: ITO/TPDPES:TBPAH (20 nm)/TAPC (35 nm)/ TCPZ:4 wt.% Ir(piq)₃ (10 nm)/TmPyBPZ (65 nm)/LiF (0.5 nm)/Al (100 nm) (\bigcirc); ITO/TPDPES:TBPAH (20 nm)/TAPC (30 nm)/TCPZ:8 wt.% Ir(PPy)₃ (10 nm)/TmPyBPZ (50 nm)/LiF (0.5 nm)/Al (100 nm) (\square); ITO/TPDP PSS:TBPAH (20 nm)/3DTAPBP (30 nm)/TCPZ:11 wt.% Ir(pr), BP4mPy (40 nm)/LiF (0.5 nm)/Al (100 nm) (∇ **v**).

based red phosphorescent OLEDs (Table 2) [10,19,20], indicating a well-balanced carrier is achieved in the EML due to the improved bipolarity of TCPZ. The emission color is deep red with an EL emission peak at 621 nm and Commission Internationale de L'Eclairage (CIE) color coordinates of (0.67, 0.33) (Fig. 9). This proves the emission directly from the triplet emitter of $Ir(piq)_3$ due to the good triplet exciton confinement on the phosphor molecules.

For the green phosphorescent OLED, ultra-low driving voltages were also achieved with a threshold voltage $(V_{\rm th})$ of 2.0 V for current and a $V_{\rm on}$ of 2.11 V for electroluminescence, which are even 0.1 V lower than the lowest driving voltages previously reported in a similar device architecture based on CBP ($V_{\text{th}} = 2.1 \text{ V}$, $V_{\text{on}} = 2.22 \text{ V}$) [7](c). In addition, driving voltages as low as 2.47 and 2.98 V were achieved at 100 and 1000 cd m^{-2} , respectively. The driving voltages are also much lower than those of the previously reported green phosphorescent OLEDs based on the other triazine derivatives as the hosts [8,9], and the reduced driving voltage can be attributed to the lower-lying LUMO energy level and the reduced exchange energy ΔE_{ST} that give an improved carrier injection into the EML. Similar to the PL spectrum of the co-deposited film of TCPZ:Ir(P-Py)3, EL spectrum of the device based on an EML of $TCPZ:Ir(PPy)_3$ is featureless with a broad band between 500 and 600 nm, indicating there is also a triplet exciplex emission in the electroluminescent process. Compared with the PL spectrum, the emission band at 560 nm is slightly higher in intensity. The EL spectrum was fitted to the emissions corresponding to $Ir(PPy)_3$ and the triplet exciplex. The emission corresponding to the triplet exciplex in the electroluminescence process is slightly stronger than that in the photoluminescence process, indicating more fraction of the triplet exciplex emission. In this system, since some carriers must be injected into the EML through the TCPZ molecules, the hole-electron recombination should lead to both Ir(PPy)₃ and TCPZ molecules in their excited states. Small difference of their triplet excited states (\sim 0.1 eV) may facilitate charge transfer between the excited states, resulting in relaxation into the exciplex state from the excited states of Ir(PPy)₃ and TCPZ. It is generally thought that the exciplex emission shows rather low efficiency. As an example, phosphorescent OLEDs based on $Ir(PPy)_3$ that yield broad structureless triplet exciplex emission between $Ir(PPy)_3$ and the host of N-2,6-dibromophenyl-1,8-naphthalimide (niBr) show a maximum η_{ext} as low as 0.3% [18]. In contrast, although the formation of the triplet exciplex, a maximum η_{ext} of 19.6% and a maximum η_P of 87.8 lm W⁻¹ were achieved in this work, and the efficiencies roll very slightly to 19.1%, 85.0 $\rm Im~W^{-1}$ and 19.1%, 70.4 Im W^{-1} at 100 and 1000 cd m^{-2} , respectively (Table 2). In addition, the efficiencies are also much higher than the previously reported Ir(PPy)₃-based green phosphorescent OLEDs utilizing the other triazine derivatives as the hosts [8,9]. Although the mechanism is slightly different, platinum complexes like platinum(II)[2-(4', 6'-difluorophenyl)pyridinato- $N, C^{2'}$](2,4-pentanedionato) (FPt) was known to have a triplet excimer emission originated from the interaction between the same molecules [21], and the optimized highest η_{ext} is near 18% that is achieved at a low brightness of 1 cd m^{-2} [21b]. For com-

Table 2	
Performance data of the phosphorescen	t OLEDs using TCPZ as the host material

Guest	V _{on} (V)	Maximum efficiency $\eta_{ m P}/\eta_{ m ext}~(m Im~W^{-1}/\%)$	At 100 cd m ⁻² $V/\eta_{\rm P}/\eta_{\rm ext}$ (V/lm W ⁻¹ /%)	At 1000 cd m ⁻² $V/\eta_{\rm P}/\eta_{\rm ext}$ (V/lm W ⁻¹ /%)
Ir(piq)₃	2.3	20.5/19.1	3.02/15.8/17.9	4.25/8.85/14.1
Ir(PPy) ₃	2.1	87.8/19.6	2.47/85.0/19.1	2.98/70.4/19.1
FIrpic	3.0	62.0/18.5	3.74/25.4/10.1	4.72/17.3/8.67
Ir(piq) ₃ and FIrpic	3.0	31.2/13.7	3.91/9.45/5.39	5.36/5.95/4.76



Fig. 9. Electroluminescent (EL) spectra of the phosphorescent OLEDs in structures: ITO/TPDPES:TBPAH (20 nm)/TAPC (35 nm)/TCPZ:4 wt.% Ir(piq)₃ (10 nm)/TmPyBPZ (65 nm)/LiF (0.5 nm)/Al (100 nm) (\bigcirc); ITO/TPDPES:TBPAH (20 nm)/TAPC (30 nm)/TCPZ:8 wt.% Ir(PPy)₃ (10 nm)/TmPyBPZ (50 nm)/LiF (0.5 nm)/Al (100 nm) (\bigcirc). The dotted lines are the fitted emissions corresponding to Ir(PPy)₃ and the triplet exciplex. ITO/TPDPES:TBPAH (20 nm)/ZDTAPBP (30 nm)/TCPZ:11 wt.% FIrpic (10 nm)/BP4mPy (40 nm)/LiF (0.5 nm)/Al (100 nm) (\bigtriangledown). The dotted lines are the fitted emissions corresponding to FIrpic and TCPZ.

parison, to our best knowledge, the current work gives the most efficient phosphorescent OLED with triplet exciplex or excimer emission hitherto.

As anticipated, different from the green and red phosphorescent OLEDs, efficiency of the phosphorescent OLED based on an EML of TCPZ:FIrpic is lower than that of the previously reported devices in a similar architecture because of the lower triplet energy of TCPZ than FIrpic, giving a maximum η_{ext} of 18.5% and a maximum η_{P} of 62.0 lm W⁻¹ [4]. Since FIrpic is more like an electron-transporter and the concentration of FIrpic is higher than that of $Ir(PPy)_3$ and $Ir(piq)_3$, effect of the host on current density is slighter than that in green and red devices. Nevertheless, current density for this device is the highest level of the previously reported blue phosphorescent OLEDs based on FIrpic. The efficiencies roll to 10.1% and 25.4 lm W^{-1} at 100 cd m^{-2} (Table 2), and the reduced efficiency can be partially attributed to the reduced carrier balance because of electron-transport property of FIrpic and low electroninjection barrier from the electron transport layer when TCPZ is utilized as the host. Different from the EL spectra of the most devices based on FIrpic reported previously [22], a broad featureless band with a maximum at 535 nm was found in addition to the FIrpic band for the device based on TCPZ (Fig. 9). Different from the PL spectrum of the co-deposited FIrpic:TCPZ film where no emission

from TCPZ was found, the new band emerging during the electroluminescent process may be attributed to the TCPZ singlet exciton formed by direct carrier recombination on the TCPZ molecules. It further proves that the carriers should be partly injected into the EML through TCPZ. Compared with the PL spectrum of the neat TCPZ film, a bathochromic shift in EL spectrum was found, and it may be attributed to its aggregation and thus the excimer emission.

Besides RGB OLEDs for display application, white OLEDs have also attracting particular attention because of its potential application in solid-state lighting. As definition, white emission requires the mixture of complementary (e.g., blue and yellow or orange) or primary colors (red, green, and blue). Generally, the white OLEDs fabricated with complementary colors exhibit color rendering index (CRI) lower than 70 due to the incomplete coverage of the whole visible region [14,23]. The emerging new band at 535 nm for the TCPZ:FIrpic-based device just covers the green-light region that lacks in a general blue/red two-color white OLED. It is thus potential to fabricate a white OLED with improved CRI by utilizing only two kinds of complementary phosphorescent emitters. To confirm this idea, a multi-emitting-layer device was fabricated in the structure of ITO/TPDPES:TBPAH (20 nm)/TAPC (30 nm)/TCPZ:11 wt.% FIrpic (4.75 nm)/TCPZ:4 wt.% Ir(piq)₃ (0.5 nm)/TCPZ:11 wt.% FIrpic (4.75 nm)/BmPyPB (40 nm)/LiF (0.5 nm)/Al (100 nm). As shown in the inset of Fig. 10(a), both its EL spectra recorded at 100 and 1000 cd m⁻² comprise an expected yellowish green band at ~540 nm combined with the bands of FIrpic and Ir(piq)₃. The CIE coordinates are (0.39, 0.45) at 100 cd m⁻², and shift slightly to (0.42, 0.46)at 1000 cd m⁻². The shift in CIE coordinates at different brightness is due to the dominate emission from TCPZ at brighter luminance, and it can be attributed to more singlet excitons of TCPZ formed by direct carrier recombination on the host molecules at higher current density. Nevertheless, although the thickness of the red-light-emitting layer is only a twentieth to that of the total emissive layers, insertion of an ultra-thin red-light-emitting layer induced sufficient red-light emission to achieve a white emission. Moreover, an improved CRI of 82 was achieved at the applicable brightness of 100 and 1000 cd m⁻². Although it might not be appropriate to be called a two-color white OLED since there is a green-light-emission from the host TCPZ, the current findings indicate that a white OLED with CRI higher than 80 can be achieved with two kinds of phosphorescent emitter, FIrpic for blue and Ir(piq)₃ for red. Considering the utilization of singlet emission from TCPZ, the current white OLED can be also called a fluorescent/phosphorescent hybrid white OLED, from which emission is



Fig. 10. (a) Current density (open) and luminance (closed) vs driving voltage characteristics and electroluminescent (EL) spectra recorded at 100 and 1000 cd m⁻² (*Inset*) and (b) external quantum efficiency (η_{ext}) (closed) and power efficiency (η_P) (open) vs luminance characteristics for the white OLED in structure: ITO/TPDPES:TBPAH (20 nm)/TAPC (30 nm)/TCPZ:11 wt.% FIrpic (4.75 nm)/TCPZ:4 wt.% Ir(piq)₃ (0.5 nm)/TCPZ:11 wt.% FIrpic (4.75 nm)/BMPyPB (40 nm)/LiF (0.5 nm)/Al (100 nm).

composed of blue and red phosphorescence and green fluorescence. It is unique since most of ever reported fluorescent/phosphorescent hybrid white OLEDs utilize green and red (or orange) phosphorescence and blue fluorescence [24]. Although its efficiency is still low ($\eta_{ext} = 5.4\%$ and $\eta_P = 9.4 \text{ Im W}^{-1}$ at 100 cd m⁻²) (Fig. 10and b), it shows us an alternative route to achieve high quality white light emission with relatively simple device architecture. We believe that optimization of device parameters could improve the efficiency further.

4. Conclusion

We report a host material containing a 1,3,5-triazine core and three phenylcarbazole arms for RGB and white phosphorescent OLEDs. Introduction of triazine as a building block of the host gives a narrow energy band-gap and a low-lying LUMO energy level due to its strong electron affinity and thus an intramolecular charge transfer between the central triazine and the carbazole periphery through the phenyl bridges. Although its singlet and triplet excited states are somewhat reduced due to this reason, a very small singlet-triplet exchange energy of 0.14 eV is achieved. Compared with the slightly reduced $E_{\rm T}$, the significantly decreased ΔE_{ST} achieved by introducing triazine as the core indicates that introducing appropriate electron donors and acceptors as building blocks of a host material is an effective route to give attractive candidates for phosphorescent OLEDs with ultra-low driving voltage as well as good triplet exciton confinement. In addition, improved bipolarity is also achieved by introducing triazine as the core and carbazole as the periphery. Transient PL measurement of Ir(PPy)₃:TCPZ films exhibits a shoulder at 565 nm whose lifetime is about two times longer than that of Ir(P- Py_{3} triplet excitons and can be attributed to the triplet exciplex formed between Ir(PPy)₃ and TCPZ. Such triplet exciplex was also found for the green phosphorescent OLED giving the most efficient phosphorescent OLED with triplet exciplex or excimer emission hitherto. Different from the PL process, a broad featureless band with a maximum at 535 nm was found for the phosphorescent OLED based on an EML of FIrpic:TCPZ, which can be attributed to the emission from the TCPZ singlet excited state formed by direct hole-electron recombination. On this base, in contrast to most of ever reported fluorescent/phosphorescent hybrid white OLEDs that utilize green and red (or orange) phosphorescence and blue fluorescence, a unique multi-emitting-layer fluorescent/phosphorescent hybrid white OLED was fabricated by introducing $Ir(piq)_3$ as a complementary red phosphorescent emitter to give a high CRI of 82. It also shows us an alternative route to achieve high quality white light emission by the utilization of the guest, host, and exciplex emission.

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