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# **Triazole and Pyridine Hybrid Molecules as Electron-Transport Materials for Highly Efficient Green Phosphorescent Organic Light-Emitting Diodes**

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**Abstract**: A series of triazole and pyridine hybrid molecules, with a triazole core and pyridine periphery, were designed and synthesized as an electron-transport layer (ETL) and a hole/exciton-block layer for green phosphorescent organic light-emitting diodes. Compared with the widely-used electron-transport material (ETM) of 3-(biphenyl-4-yl)-5-(4-*tert*-butylphenyl)-4-phenyl-4H-1,2,4-triazole (TAZ) with a triazole core, lower-lying HOMO and LUMO energy levels were obtained with the introduction of pyridine rings onto the pe-

riphery of the molecules, giving improved electron injection and carrier confinement. Significantly reduced driving voltages were achieved in a device structure of ITO/HATCN (5 nm)/TAPC (40 nm)/CBP:8 wt%  $Ir(PPy)_3$  (10 nm)/ETL (40 nm)/LiF (1 nm)/Al (90 nm), giving a maximum power efficiency of 72.2  $ImW^{-1}$  and an external quantum efficiency of 21.8%, due to the improved electron injection and transport and thus, more balanced carrier recombination, which are much higher than those of the device based on TAZ.

Keywords: charge carrier injection · electron transport · hybrid molecules · organic light-emitting diodes · triazole derivatives

### 1. Introduction

The performance of organic light-emitting diodes (OLEDs) has been greatly improved<sup>[1]</sup> since Tang and his coworkers made a huge breakthrough by advancing the efficiency of OLEDs to 1%.<sup>[2]</sup> OLEDs with high efficiency have been reported by many groups<sup>[3]</sup> since then. Phosphorescent OLEDs using phosphorescent dyes doped into charge-transporting hosts as emissive layers (EMLs)<sup>[4]</sup> have attracted extensive attention due to their highly efficient emission, compared with conventional fluorescent OLEDs, on account of collecting both singlet and triplet excitons. Generally, balanced carrier recombination plays a critical role in achieving high efficiency OLEDs. Since the electron-transport ability of organic materials is usually poorer than their hole-transport ability, electron-transport materials (ETMs), with high electron-injection and -transport abilities, are required to give balanced carriers, and thus improve OLED performance.<sup>[5]</sup> Kido et al. have developed a highly conductive n-doped electron-transport layer (ETL) by co-evaporating ETMs and highly active alkaline metals such as Li<sup>[6]</sup> to obtain an effective electron injection and transport in OLEDs. In this case, an exciton-block layer (EBL) is required to prevent penetration of n-dopants into the EML and thus exciton quenching. The additional layer will lead to the complexity of the device fabrication, and this may increase the cost for applications in flat-panel displays and lighting.

To obtain high electron-injection and -transport materials, pyrimidine,<sup>[7]</sup> phenanthroline<sup>[8]</sup>, pyridine<sup>[5,7d,e,9]</sup> and other heteroaromatic groups with high electron affinity were introduced into  $\pi$ -conjugated systems. As a compound with a five-membered heteroaromatic triazole core, TAZ [3-(biphenyl-4-yl)-5-(4-*tert*-butylphenyl)-4-phenyl-4H-1,2,4-triazole] is widely used as an ETM.<sup>[10]</sup> However, good performance could be hardly achieved for the devices with TAZ as an ETL because of its poor electron-transport ability.<sup>[11]</sup> This drawback limits its further application in high performance OLEDs. It was found that the LUMO (lowest unoccupied molecular orbital) energy level of the six-membered pyridine ring is deeper

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than that of the C=N containing five-membered heteroaromatic compounds, leading to better electron injection.<sup>[12]</sup> The phenylpyridine<sup>[7d,9b]</sup> moiety can be used to construct ETMs with high electron-transport ability<sup>[9d,13]</sup> and high triplet energy ( $E_T$ ).<sup>[5]</sup> In addition, excellent ETMs were developed with the combination of pyridine ring as the periphery and benzene<sup>[5]</sup> or triazine<sup>[14]</sup> as the core, and the ETMs with a pyrid-3-yl periphery were confirmed to give better device performance.<sup>[14,15]</sup>

In this article, we report a series of triazole and pyridine hybrid molecules with triazole as the core and pyridine as the periphery (Figure 1), which exhibit obviously



**Figure 1.** Molecular structures of the designed triazole and pyridine hybrid molecules TPyTAZp, TPyTAZm, TPyBnTAZp, and TPyBnTAZm. Also shown the molecular structure of TAZ for comparison.

better electron injection and transport than TAZ. Highly efficient green phosphorescent OLEDs, with reduced efficiency roll-off, were achieved with these molecules as the ETLs, due to their good confinement of both carriers and excitons within the EML, giving a maximum power efficiency (PE<sub>max</sub>) of 72.2 lm  $W^{-1}$ , and an external quantum efficiency (EQE<sub>max</sub>) of 21.8%. In addition, extremely reduced driving voltages were obtained for the hybrid molecules, in comparison with TAZ. The lowest turn-on voltage  $(V_{on})$  (at the luminance of 1 cd m<sup>-2</sup>) of 2.5 V was achieved for the device based on TPyTAZp, which is much lower than that of the device based on TAZ (4.1 V). However, when a p-doped hole injection layer is not used, the current  $V_{\mbox{\scriptsize on}}$  value is even lower than that of the device based on a p-doped polymer hole injection layer and a classic ETM of TpPyPB (1,3,5-tri(p-pyrid-3-yl-phenyl)benzene) with a benzene core.<sup>[5]</sup> Their structure-property relationships, including the thermal and electrochemical properties; electron-transport properties in electrononly devices; and current density-voltage-luminance (J-V-L) characteristics of phosphorescent OLEDs, were studied comprehensively.

### 2. Results and Discussion

#### 2.1 Thermal and Photophysical Properties

As can be clearly seen from Figure 2, TPyTAZm and TPyBnTAZm possess distinct glass-transition temperatures ( $T_g$ ) of 77 and 94 °C, respectively. In contrast, when the three meta-connected benzene rings are changed to para-connection, the enhanced molecular rigidity of TPyBnTAZp leads to difficulty in the movement of the molecular segments, and thus its  $T_g$  increases to 112 °C. Similar to TAZ, TPyTAZp exhibits an amorphous state up to 200 °C, maybe due to its most rigid molecular structure. In addition, the current triazole and pyridine hybrid molecules exhibit excellent thermal stability, with decomposition temperatures ( $T_d$ ) ranging from 450 to 510 °C, which is far higher than that of TAZ (298 °C).

As shown in Figure 3, the absorption spectrum of TPy-TAZp, based on a p-triphenyltriazole core, peaks at 300 nm in toluene solution. With three more meta-connected benzene rings, the absorption peak of TPyBn-TAZp blue-shifts to 285 nm, accompanied with a shoulder at 300 nm, due to the weakened conjugation. For the two molecules based on a m-triphenyltriazole core, the absorption peak of TPyTAZm with a peripheral pyridine ring is at 283 nm. In comparison, TPyBnTAZm, with a peripheral pyridyl-benzene, red-shifts to 290 nm. This phenomenon indicates that TPyBnTAZm, with peripheral meta-connected benzene rings, have longer a conjugated length than TPyTAZm. Compared with the absorption spectra in toluene solutions, the absorption peaks of all the molecules in thin solid films do not change obviously. Meanwhile, TPyTAZm and TPyBnTAZm have relatively narrower absorption ranges than TPyTAZp and TPyBn-TAZp, because of their poorer conjugation.



**Figure 2.** Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (inset) characteristics of TPyTAZp, TPyTAZm, TPyBnTAZp, and TPyBnTAZm.



**Figure 3.** Room temperature UV-vis absorption (solid) and photoluminescent (PL) (open) spectra of TPyTAZp ( $\mathbf{\nabla}$ ), TPyTAZm ( $\mathbf{\Theta}$ ), TPyBnTAZp ( $\mathbf{\Delta}$ ) and TPyBnTAZm ( $\mathbf{\Box}$ ) in toluene solutions (bottom) and thin solid films (top) on quartz substrates.

Similar to the absorption spectra, bathochromic shifts were also observed for the PL spectra recorded in both toluene solutions and thin solid film states. PL spectra of TPyTAZp and TPyBnTAZp peak at 372 and 385 nm in toluene solution, respectively. While the emission peaks of TPyTAZm and TPyBnTAZm are at 349 and 348 nm, respectively, which show smaller stoke shifts and narrower full-widths at half maximum than TPyTAZp and TPyBnTAZp. As compared with the PL spectra in toluene solutions, the PL spectra of TPyTAZm and TPyBnTAZm are greatly red-shifted, which may be ascribed to the intense aggregation in solid films.

#### 2.2 Electrochemical Properties and DFT Calculations

The electrochemical properties of the triazole and pyridine hybrid molecules were measured by cyclic voltammetry in dichloromethane solutions (Figure 4). The onsets of oxidation potentials ( $E_{ox}$ ) and reduction poten-



**Figure 4.** Cyclic voltammograms of TPyTAZp, TPyTAZm, TPyBn-TAZp, and TPyBnTAZm in dichloromethane solutions.

tials ( $E_{red}$ ) for TPyTAZp, TPyTAZm, TPyBnTAZp and TPyBnTAZm were found to be 1.87/-1.67, 1.84/-1.63, 1.82/-1.62, and 1.89/-1.70 V, respectively. Under the same experimental conditions, the redox potential  $(E_{1/2})$ of ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) was measured to be 0.40 V. The redox potential of Fc/Fc<sup>+</sup> has an absolute energy level of -4.80 eV, compared with the vacuum level.<sup>[16]</sup> Therefore, the HOMO (highest occupied molecular orbital) and LUMO energy levels of the current materials are calculated according to the following equations: HOMO =  $-e (E_{ox} + 4.40)$  V, LUMO =  $-e (E_{red} + 4.40)$  V. Due to the introduction of strong electrophilic pyridine rings onto the periphery of the molecules, much lower LUMO energy levels are achieved in comparison with the -2.7 eV of TAZ. Such deep LUMO energy levels are beneficial for electron injection and transport.

To get further insights into the molecular orbitals of the pyridine and triazole hybrid molecules, density functional theory (DFT) calculations were also performed with the B3LYP/6-311G + dp basis set, using the Gaussian suite of programs (Gaussian 03W). The calculated

Table 1. Physical properties of the triazole-core-containing materials.

Materials	T <sup>[a]</sup> (°C)	T <sub>d</sub> <sup>[b]</sup> (°C)	E <sup>opt [c]</sup> (eV)	HOMO <sup>[d]</sup> (eV)	LUMO <sup>[e]</sup> (eV)	Е <sub>номо</sub> <sup>[f]</sup> (eV)	E <sub>LUMO</sub> <sup>[f]</sup> (eV)	E <sup>cal [g]</sup> (eV)	E <sub>T</sub> <sup>cal [g</sup> (eV)
 TPyTAZp	_	458	3.32 (3.59)	-6.27	-2.73	-6.40	-2.03	4.37	2.57
TPyTAZm	77	450	3.80 (4.05)	-6.24	-2.77	-6.22	-2.09	4.12	2.77
TPyBnTAZp	112	498	3.42 (3.62)	-6.22	-2.78	-6.04	-1.95	4.09	2.57
TPyBnTAZm	94	510	3.72 (3.95)	-6.29	-2.70	-6.24	-1.86	4.38	2.78
TAZ	-	298	-	-6.3 <sup>[1]</sup>	-2.7 <sup>[1]</sup>	-5.97	-1.62	4.35	2.58

[a]  $T_g$  was measured by DSC. [b] The decomposition temperature ( $T_d$ ) was measured by TGA with 5% weight-loss. [c] The optical band gap corresponding to the lowest-energy absorption edge of the UV-vis absorption spectrum of the material in thin solid film and in toluene solution (in parentheses). [d] HOMO = -e ( $4.40 + E_{ox}$ ) V. [e] LUMO = -e ( $4.40 + E_{red}$ ) V. [f] HOMO and LUMO energy levels obtained by DFT calculations (B3LYP/6-311G+dp) (Gaussian 03W). [g] Calculated energy band gap ( $E_g^{cal} = |E_{HOMO}| - |E_{LUMO}|)$  and triplet energy ( $E_T^{cal}$ ).

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HOMO and LUMO energy levels, energy band gaps  $(E_g^{cal})$ , and triplet energy levels  $(E_T^{cal})$  of the molecules are listed in Table 1. Though the calculated values are somewhat different from the experimental values, a similar trend is observed.

#### 2.3 OLED Characterization

To evaluate the electron-injection/-transport abilities of the developed triazole and pyridine hybrid molecules, green phosphorescent OLEDs were fabricated with  $Ir(PPy)_3$  as the phosphorescent emitter. Table 2 gives a summary of the device performance. Figure 5 presents the current density-voltage-luminance (*J-V-L*) characteristics. Compared with the device based on TAZ, the *J-V* and *L-V* curves of the other devices feature steeper increments, indicating the improved electron injection and transport by the developed ETMs.



**Figure 5.** Current density and luminance versus driving voltage (*J*-*V*-*L*) characteristics of the green phosphorescent OLEDs in a structure of ITO/HATCN (5 nm)/TAPC (40 nm)/CBP:8 wt%  $Ir(PPy)_3$  (10 nm)/TPyTAZp ( $\bigtriangledown \bigtriangledown$ ), TPyTAZm ( $\odot$ ), TPyBnTAZp ( $\bigstar \bigtriangleup$ ) and TPyBnTAZm ( $\blacksquare$ ) or TAZ ( $\diamondsuit$ ) (40 nm)/LiF (1.0 nm)/Al(90 nm).

As shown in Table 2, the device based on TPyTAZp exhibits a low  $V_{on}$  of 2.5 V, and driving voltages of 3.0 and 3.7 V at 100 and 1000 cd m<sup>-2</sup>, respectively. All are much lower than the previously reported values based on Ir(PPy)<sub>3</sub> with the widely used ETM of 1,3,5-tri((3-pyridyl)-phen-3-yl) benzene (TmPyPB)<sup>[5]</sup> as the ETL, probably due to the improved electron injection. Its Von is even lower than that of the device based on TpPyPB,<sup>[5]</sup> although no p-doped hole injection layer was used for the current devices. Compared with the device based on TPy-TAZp, the Von of the devices based on TPyTAZm, TPyBnTAZp and TPyBnTAZm increase to 2.9, 4.0, and 3.0 V, with driving voltages of 3.6, 5.4, and 4.0 V at  $100\ cd\ m^{-2}\!,$  and 4.5, 6.5, and 5.1 V at  $1000\ cd\ m^{-2}\!,$  respectively. To further understand this phenomenon, electrononly devices were fabricated with a configuration of ITO/ LiF (1 nm)/ETMs (50 nm)/LiF (1 nm)/Al (80 nm). Their current density-voltage (J-V) characteristics are shown in Figure 6. The devices based on the pyridine-containing ETMs show much higher current density than that of the device based on TAZ at the same bias, indicating they



**Figure 6.** Current density-voltage (*J-V*) characteristics of the electron-only devices based on TPyTAZp ( $\bigtriangledown$ ), TPyTAZm ( $\bigcirc$ ), TPyBnTAZp ( $\blacktriangle$ ) and TPyBnTAZm ( $\blacksquare$ ), TAZ ( $\diamondsuit$ ) in a structure of ITO/LiF (1 nm)/ETMs (50 nm)/LiF (1 nm)/AI (80 nm).

**Table 2.** Summary of the electroluminescent performance of the devices in a structure of ITO/HATCN (5 nm)/TAPC (40 nm)/CBP:8 wt%  $Ir(PPy)_3$  (10 nm)/ETMs (40 nm)/LiF (1 nm)/Al (90 nm).

ETMs	V <sub>on</sub> <sup>[a]</sup> (V)	CE <sub>max</sub> (cd A <sup>-1</sup> )	PE <sub>max</sub> (Im W <sup>-1</sup> )	EQE <sub>max</sub> (%)	at 100 cd m <sup>-2</sup>				at 1000 cd m <sup>-2</sup>			
					V (V)	CE (cd A <sup>-1</sup> )	PE (lm W <sup>-1</sup> )	EQE (%)	V (V)	CE (cd A <sup>-1</sup> )	PE (lm W <sup>-1</sup> )	EQE (%)
TPyTAZp	2.5	51.9	58.2	15.5	3.0	51.7	53.3	15.4	3.7	46.7	40.1	13.9
TPyTAZm	2.9	73.6	72.2	21.8	3.6	67.8	58.3	20.0	4.5	60.2	42.3	17.9
TPyBnTAZp	4.0	30.5	30.1	9.1	5.4	30.4	17.9	9.0	6.5	29.5	14.1	8.8
TPyBnTAZm	3.0	52.8	53.3	16.1	4.0	50.8	39.8	15.1	5.1	44.2	27.3	13.1
TAZ	4.1	57.3	36.0	17.1	5.6	53.9	30.4	16.0	7.2	43.9	19.1	13.1

[a] at the luminance of 1 cd  $m^{-2}$ .

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have better electron-injection and -transport abilities than TAZ due to their deeper LUMO energy levels, as well as stronger electron affinity.  $V_{on}$  shows the same trend as the electron-injection and -transport abilities of the pyridine-containing ETMs.

Although TPyTAZp has the best electron-transport ability in both light-emitting devices and electron-only devices, its phosphorescent OLEDs exhibit a maximum current efficiency ( $CE_{max}$ ) of only 51.9 cd A<sup>-1</sup> and a maximum power efficiency ( $PE_{max}$ ) of 58.2 lm W<sup>-1</sup>; both are much lower than those of the devices based on TPy-TAZm (73.6 cd A<sup>-1</sup> and 72.2 lm W<sup>-1</sup>). This may be attributed to the reduced charge-carrier balance, since TPy-TAZp has excellent electron-injection and -transport abilities, which may lead to excess electrons in the EML. Among them, TPyTAZm shows the best performance (see Figure 7), and its EQE<sub>max</sub> approaches 21.8%. In ad-



**Figure 7.** Current and power efficiency versus luminance (top) and external quantum efficiency versus luminance characteristics (bottom) of the green phosphorescent OLEDs in a structure of ITO/ HATCN (5 nm)/TAPC (40 nm)/CBP:8 wt% Ir(PPy)<sub>3</sub> (10 nm)/TPyTAZp ( $\bigtriangledown$ ), TPyTAZm ( $\bigcirc$ ), TPyBnTAZp ( $\bigstar$ ) and TPyBnTAZm ( $\blacksquare$ )) or TAZ ( $\diamondsuit$ ) (40 nm)/LiF (1.0 nm)/Al(90 nm).

dition, the EQE is as high as 17.9%, even at a brightness of 1000 cdm<sup>-2</sup> (4.5 V). Aside from the balanced carrier flux, considering the relatively higher  $E_{\rm T}^{\rm cal}$  of TPyTAZm, the improved performance may be also attributed to the improved exciton confinement within the emission layer, even at high current density. Compared with TPyTAZm, TPyBnTAZm, with three more meta-connected phenyls, has almost the same electron-injection and -transport abilities and  $E_{\rm T}^{\rm cal}$ , but gives much lower efficiency. Taking the LUMO energy levels of the emitting layer into account, the LUMO-LUMO offset at the interface between CBP (LUMO=-2.9 eV)<sup>[17]</sup> and TPyTAZm is 0.13 eV, while the LUMO-LUMO offset at the interface between CBP and TPyBnTAZm is 0.20 eV. Thereby, the electron transport into the EML from TPyTAZm may be easier than that from TPyBnTAZm. Accordingly, current density in the light-emitting devices exhibits the same behavior, to give improved carrier balance and thus, improved efficiency.

Similar to typical phosphorescent OLEDs, efficiency roll-off at high driving-current density is also observed here. However, power efficiencies for the TPyTAZpbased device remain above 53 and 40  $\text{Im W}^{-1}$ , at the practical brightnesses of 100 and 1000  $\text{cd m}^{-2}$ , respectively, which are much higher than those of the device based on TAZ (Figure 7). The higher power efficiencies for the device based on TPyTAZp should arise from its significantly reduced driving voltage at the same brightness, owing to its better electron injection and transport. Power efficiencies are further improved to  $58.3 \text{ lm W}^{-1}$  at  $100 \text{ cd m}^{-2}$  and  $42.3 \text{ lm W}^{-1}$  at  $1000 \text{ cd m}^{-2}$  when the linkage position of benzene rings changes from the para position to the meta position. As shown in Table 1, TPy-TAZm possesses higher  $E_{\rm T}^{\rm cal}$  than TPyTAZp. The improved efficiency may also be attributed to the improved confinement of Ir(PPy)<sub>3</sub> triplet excitons by the adjacent TPyTAZm, compared with TPyTAZp, as well as the increased carrier balance. Power efficiency of 39.8 lm W<sup>-1</sup> was achieved at the luminance of  $100 \text{ cd m}^{-2}$  for the TPvBnTAZm-based device. Athought it is lower than that of the devices based on TPyTAZp or TPyTAZm, it still shows a high EQE over 15%. As shown in Figure 7, reduced roll-off in EQE can be achieved by the developed ETMs, compared with that of TAZ. As mentioned above, since the triplet excitons could be well confined within the EML, when the developed ETMs were used as an ETL as well as a hole/exciton-block layer, the reduced efficiency roll-off may also have arisen from good exciton confinement. It is quite interesting that reduced efficiency roll-off can be achieved solely by using an ETM with enhanced triplet exciton confinement as an ETL and a hole/ exciton-block layer. This suggests that efficiency roll-off may also arise from triplet-exciton or carrier-exciton quenching by the adjacent ETMs, as well as from the usually reported triplet-triplet annihilation.

All of the current devices exhibit similar EL spectra, which peak at 512 nm (Figure 8), and no emission from the ETL was found, further indicating that carriers and excitons are completely confined within the EML.

### 3. Conclusion

A series of triazole and pyridine hybrid molecules were successfully synthesized using typical Suzuki cross-coupling reactions, and their thermal, photophysical and electrochemical properties were thoroughly studied. Their HOMO and LUMO energy levels were strongly dependent on the linkage position and the number of benzene



**Figure 8.** EL spectra of the green phosphorescent OLEDs in a structure of ITO/HATCN (5 nm)/TAPC(40 nm)/CBP:8 wt%  $Ir(PPy)_3$  (10 nm)/TPyTAZp ( $\checkmark$ ), TPyTAZm ( $\bigcirc$ ), TPyBnTAZp ( $\blacktriangle$ ) and TPyBnTAZm ( $\blacksquare$ ) or TAZ( $\diamondsuit$ ) (40 nm)/LiF (1.0 nm)/AI (90 nm) measured at a driving current density of 10 mA cm<sup>-2</sup>.

rings. By using these molecules as an ETL and a hole/exciton-block layer in green phosphorescent OLEDs, much better electron-injection/-transport abilities were achieved, which gave significantly reduced driving voltages. compared with the widely used ETM of TAZ, due to the introduction of strongly electrophilic pyridine rings on the periphery of the molecules. The device based on TPy-TAZm exhibited the highest efficiency, with a PE<sub>max</sub> of up to  $73.6 \text{ lm W}^{-1}$  (72.2 cd A<sup>-1</sup>, 21.8%), due to the matched energy levels, high electron-transport ability, and more balanced carrier recombination. In addition, compared with the device based on TAZ, it showed much higher PEs of 58.3 and 42.3 lm W<sup>-1</sup>, at the practical brightnesses of 100 and 1000  $cdm^{-2}$ , due to its good triplet exciton confinement ability and reduced efficiency roll-off. The current findings are beneficial to the design of triazolebased ETMs for the further improvement of phosphorescent OLEDs.

#### 4. Experimental Section

#### 4.1 General

<sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were measured using a Bruker AV-300 spectrometer. Mass spectrometry (MS) data were obtained on a Waters TQD. Cyclic voltammetry (CV) measurements were carried out in dichloromethane by using  $Bu_4NPF_6$  (0.1 M) as an electrolyte on a CHI600D electrochemical workstation with a graphite working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. UV-vis absorption spectra were recorded on a HP 8453 spectrophotometer. PL spectra were recorded on a FL-3 spectrofluorometer (HORIBA). DSC measurements were carried out with a NETZSCH DSC 204 under a nitrogen flow at a heating rate of  $10^{\circ}$ Cmin<sup>-1</sup>. TGAs were conducted on a NETZSCH TG 209 under a nitrogen flow rate of 20 ml min<sup>-1</sup> at a heating rate of  $10^{\circ}$ Cmin<sup>-1</sup>.

#### 4.2 Materials

All materials were obtained from commercial suppliers and used without further purification unless otherwise noted. Scheme 1 depicts the synthetic routes of the designed triazole and pyridine hybrid molecules.



**Scheme 1.** Synthetic routes of TPyTAZp, TPyTAZm, TPyBnTAZp, and TPyBnTAZm. Reagents and conditions: i)  $N_2H_4$ · $H_2O$ , NMP, r. t. ; ii) PCl<sub>5</sub>, toluene, reflux; iii) *p*-bromoaniline or *m*-bromoaniline, N,N-dimethylaniline, 135°; iv) Pd(PPh<sub>3</sub>)<sub>4</sub>, 2 M K<sub>2</sub>CO<sub>3</sub>, toluene/ethanol, 95°.

1,2-bis(4-bromophenyl)hydrazine (2): 4-Bromobenzoyl chloride (2.6 g, 12 mmol) was dissolved in 30 ml of Nmethylpyrrolidone (NMP) in a double-necked flask, and then hydrazine hydrate (0.30 g, 6 mmol) was added dropwise into the solution. The reaction mixture was stirred at room temperature overnight and then poured into 200 ml deionized water. The precipitate was collected by filtration through a funnel. The collected solid was washed using deionized water, ethyl acetate, and anhydrous ethanol in sequence, then dried under vacuum to give **2** (1.83 g, 76.6%) as a white solid. <sup>1</sup>H NMR (300 MHz, DMSO-*d*6,  $\delta$ , ppm): 10.65 (s, 2H), 7.84 (d, 4H ), 7.74 (d, 4H).

1,2-bi(chloro(4-bromophenyl)methylene)hydrazine (3): 2 (0.84 g, 2.1 mmol) and phosphorus pentachloride (PCl<sub>5</sub>) (0.96 g, 4.62 mmol) were dissolved in 20 ml of anhydrous toluene with agitation and refluxed under a flow of nitrogen for 5 h. After being cooled to room temperature, water was added to quench the reaction, and the mixture

was extracted with dichloromethane. The combined organic phase was washed with saturated brine and dried over MgSO<sub>4</sub>. The subjection of the crude product to silica gel chromatography afforded **3** (0.73 g, 80.0%) as a pale yellow solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.00 (d, 4H), 7.60 (d, 4H).

3,4,5-tri(4-bromophenyl)-4H-1,2,4-triazole (4): 3 (0.86 g, 2.0 mmol) and *p*-bromoaniline (0.34 g, 2.0 mmol) were dissolved in 15 ml of N,N-dimethylaniline and stirred at 135 °C for 12 h under a flow of nitrogen. After being cooled to room temperature, HCl (30 ml, 2 M) was added with agitation for 30 min, and then the mixture was filtered through a Buchner funnel. The subjection of the crude product to silica gel chromatography afforded **4** (0.63 g, 58.6%) as a white solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.60 (d, 2H), 7.49 (d, 4H), 7.25 (d, 4H), 7.02 (d, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 153.94, 133.68, 133.61, 131.95, 130.19, 129.16, 125.30, 124.71, 124.25.

3,4,5-tri(4-pyrid-3-yl-phenyl)-4H-1,2,4-triazole (TPy-TAZp): 4 (1.10 g, 2.1 mmol), pyrid-3-yl boronic acid (1.08 g, 8.64 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (84 mg, 0.073 mmol), and 2 M aqueous potassium carbonate (20 ml) in toluene (50 ml) and ethanol (20 ml) was stirred at 95 °C for 24 h under argon atmosphere. After being cooled to room temperature, water was added to quench the reaction, and the mixture was extracted with dichloromethane. The combined organic phase was washed with saturated brine and dried over MgSO<sub>4</sub>. The subjection of the crude product to silica gel chromatography afforded TPyTAZp (0.94 g, 94.7%) as a white solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 9.10–8.47 (m, 5H), 7.96 (d, 1H), 7.88 (d, 2H), 7.73 (d, 2H), 7.62–7.52 (m, 9H), 7.48–7.30 (m, 5H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ, ppm): 154.44, 149.43, 148.96, 148.08, 139.41, 139.11, 134.93, 134.35, 134.23, 129.41, 128.70, 128.55, 127.19, 126.48, 123.84. Calcd. C<sub>35</sub>H<sub>24</sub>N<sub>6</sub> 528.6, APCI<sup>+</sup>-MS (m/z): 529.3 (M<sup>+</sup>).

3,4,5-tri(4-(3-pyrid-3-yl-phenyl)-phenyl)-4H-1,2,4-triazole (TPyBnTAZp): TPyBnTAZp was synthesized in a similar manner to TPyTAZp. Yield: 76.5%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.88 (s, 3H), 8.62 (s, 3H), 7.98–7.92 (m, 3H), 7.84 (s, 1H), 7.80 (s, 1H), 7.76 (s, 3H), 7.72–7.68 (m, 1H), 7.62–7.60 (m, 12H), 7.57 (s, 3H), 7.55 (s, 1H), 7.45–7.38 (m, 4H), 7.35 (s, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 154.60, 148.84, 148.67, 148.30, 142.10, 141.90, 140.88, 140.00, 138.81, 138.55, 136.44, 136.27, 134.59, 134.52, 129.89, 129.68, 129.29, 128.72, 128.37, 127.26, 127.10, 126.87, 126.83, 126.66, 126.08, 126.02, 125.95, 123.68, 123.63. Calcd. C<sub>53</sub>H<sub>36</sub>N<sub>6</sub> 756.9, APCI<sup>+</sup>-MS (m/z): 757.4 (M<sup>+</sup>).

1,2-bis(3-bromophenyl)hydrazine (6): 6 was synthesized in a similar manner to 2. Yield: 75.3%. <sup>1</sup>H NMR (300 MHz, DMSO-d6,  $\delta$ , ppm): 10.71 (s, 2H), 8.09 (s, 2H), 7.92 (d, 2H), 7.82 (d, 2H), 7.51 (t, 2H).

1,2-bi(chloro(3-bromophenyl)methylene)hydrazine (7): 7 was synthesized in a similar manner to 3. Yield: 98.3%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 8.27 (s, 2H), 8.06 (d, 2H), 7.67 (d, 2H), 7.36 (t, 2H).

3,4,5-tri(3-bromophenyl)-4H-1,2,4-triazole (8): 8 was synthesized in a similar manner to 4. Yield: 77.5%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.80 (s, 3H), 7.53 (d, 2H), 7.41–7.32 (m, 2H), 7.30–7.11 (m, 5H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 153.49, 135.71, 133.49, 133.11, 131.86, 131.45, 130.64, 130.04, 128.16, 126.98, 126.52, 123.56, 122.74.

Synthesis of 3,4,5-tri(3-pyrid-3-yl-phenyl)-4H-1,2,4-triazole (TPyTAZm): TPyTAZm was synthesized in a similar manner to TPyTAZp. Yield: 87.1 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.64–8.55 (m, 6H), 7.82–7.78 (d, 1H), 7.76 (t, 1H), 7.74 (t, 1H), 7.73–7.70 (m, 2H), 7.69 (s, 1H), 7.67 (s, 1H), 7.65–7.62 (m, 1H), 7.60 (t, 1H), 7.56 (t, 1H), 7.53 (m, 1H), 7.49 (s, 1H), 7.46 (s, 1H), 7.45–7.43 (m, 1H), 7.37–7.30 (m, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 154.44, 149.58, 148.91, 148.09, 148.03, 140.43, 138.15, 136.08, 135.54, 134.48, 134.38, 134.27, 131.11, 129.45, 128.60, 128.54, 128.36, 127.59, 127.50, 127.35, 126.49, 123.81, 123.62. Calcd. C<sub>35</sub>H<sub>24</sub>N<sub>6</sub> 528.6, APCI<sup>+</sup>-MS (m/z): 529.2 (M<sup>+</sup>).

3,4,5-tri(3-(3-pyrid-3-yl-phenyl)-phenyl)-4H-1,2,4-triazole (TPyBnTAZm): TPyBnTAZm was synthesized in a similar manner of TPyTAZp. Yield: 79.7%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.78 (s, 2H), 8.75 (s, 1H), 8.63–8.57 (m, 3H), 7.88 (d, 2H), 7.85–7.77 (m, 2H), 7.68 (s, 4H), 7.67–7.64 (m, 3H), 7.54–7.45 (m, 11H), 7.43–7.38 (m, 4H), 7.35–7.28 (m, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 154.57, 148.47, 148.14, 143.12, 141.05, 140.86, 139.77, 138.69, 138.45, 136.44, 136.08, 134.58, 134.47, 130.72, 129.82, 129.60, 129.31, 128.63, 128.54, 128.20, 127.59, 127.43, 127.05, 126.82, 126.76, 126.66, 126.50, 125.85, 123.58. Calcd. C<sub>53</sub>H<sub>36</sub>N<sub>6</sub> 756.9, APCI<sup>+</sup>-MS (m/z): 757.4 (M<sup>+</sup>).

#### 4.3 Device Fabrication and Characterization

Glass substrates pre-coated with a 170 nm, thin layer of indium tin oxide (ITO) with a sheet resistance of  $10 \Omega$ per square meter were thoroughly cleaned in an ultrasonic bath of acetone, isopropyl alcohol, detergent, deionized water, isopropyl alcohol, and treated with O<sub>2</sub> plasma, for 20 min in sequence. Organic layers were deposited onto the ITO-coated substrates by high-vacuum ( $< 5 \times 10^{-4}$  Pa) thermal evaporation. A 5 nm, thin layer of dipyrazino (2,3-f:2',3'-h)quinoxaline-2,3,6,7,10,11-hexacarbonitrile (HATCN) was deposited to improve the hole injection from the anode. Then, a 40 nm, thin hole-transport layer of di-(4-(N,N-ditolyl-amino)-phenyl)cyclohexane (TAPC) was deposited. Next, 8 wt % tris(2phenylpyridine)iridium(III) (Ir(PPy)<sub>3</sub>) was co-deposited with 4,4'-bis(carbazol-9-yl)biphenyl (CBP) to form a 10 nm, thin EML. Finally, a 40 nm, thin ETL of TAZ, TPyTAZp, TPyTAZm, TPyBnTAZp or TPyBnTAZm was deposited to transport electrons, block holes and to

confine excitons in the emission zone. Cathodes, consisting of a 1 nm, thin layer of LiF followed by a 90 nm, thin layer of Al, were patterned using a shadow mask with an array of 3 mm × 3 mm openings. Deposition rates are 1– 2 Å s<sup>-1</sup> for organic materials, 0.1 Å s<sup>-1</sup> for LiF, and 6 Å s<sup>-1</sup> for Al, respectively. Electroluminescent (EL) spectra were taken by an optical analyzer, Photo Research PR705. The current density and luminance versus driving voltage characteristics were measured by Keithley 2420 and Konica Minolta chromometer CS-200, respectively.

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