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Rational Utilization of Intramolecular and Intermolecular Hydrogen Bonds to Achieve Desirable Electron Transporting Materials with High Mobility and High Triplet Energy

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Three new pyrimidine-containing star-shaped compounds, namely, 1,3,5-tri(3-(pyrimidin-5-yl)phenyl)benzene (**TPM-TPB**), 2,4,6-tris(3-(pyrimidin-5-yl)phenyl)-1,2,5-triazine (**TPM-TAZ**) and 3,5,6-tris(3-(pyrimidin-5-yl)phenyl)-1,2,4-triazine (**TPM-i-TAZ**) were synthesized and characterized. These new compounds exhibited favorable electronic affinity ($E_a > 2.81 \text{ eV}$) and the triplet energy levels (E_T) up to ~ 2.83 eV. X-ray diffraction analysis of the compounds revealed that the intramolecular and intermolecular C-H⁻⁻N hydrogen bonds of **TPM-TAZ** resulted in high electron mobility up to 2.0 × 10⁻³ cm² V⁻¹ s⁻¹. Using these compounds as the electron transporting materials, the blue phosphorescent organic lightemitting devices showed good performance, with a very low turn-on voltage of 2.4 V, a maximum current efficiency of 26.9 km V⁻¹.

Introduction

Organic light-emitting devices (OLEDs) unveil a bright future for commercial application as the next generation full-color flat-panel displays and illumination sources.¹ Despite great achievements in red and green electroluminescent devices, high efficiency blue OLEDs are still remains to be explored.² The lack of suitable electron transporting materials (ETMs) for blue emission is one of the critical factors for the inferior device performances.³ Since the ETMs for blue emission devices should have both high triplet energy levels ($E_{\rm T}$ s) to confine the excitons in the emitting layer and high electronic mobility ($\mu_{\rm e}$) for charge carrier transport.⁴ Although high $E_{\rm T}$ s molecules would be readily achieved by breaking the π -conjugation *via* sp^3 hybridized C, Si, P atoms, etc,⁵ the twisted molecular configurations are usually disadvantageous for the $\mu_{\rm e}$ s of the materials.⁶

Recently, Kido and coworkers reported some phenylpyridine-based ETMs *via meta*-positions π -extension, which simultaneously achieved high $E_{\rm T}$ (> 2.7 eV) and high $\mu_{\rm e}$ (~ 1 × 10⁻³ cm² V⁻¹ s⁻¹).⁷ It is supposed that the intermolecular

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^c State Key Laboratory of Supramolecular Structure and Materials, Department of Chemistry, Jilin University, Changchun, 130012, People's Republic of China. *E-mail: lifenq01@jlu.edu.cn. C-H^{...}N hydrogen bonds formed in vacuum-deposited films facilitate the horizontal molecular orientation,⁸ consequently cause an increase of π - π overlap between the adjacent molecules and a decrease of the positional disorder in the film.⁹ This improves the charge transport characteristics of the film.



Fig. 1 Schematic diagram of the molecular design strategy.

Compared to the pyridine unit, pyrimidine or triazine moieties would provide more sites to form C-H^{...}N hydrogen bonds, as well as more favorable electron affinity and thermostability.¹⁰ Therefore, on the basis of pyrimidine and triazine, we designed and synthesized three new star-shaped ETMs, namely **TPM-TPB**, **TPM-TAZ** and **TPM-i-TAZ** (Fig. 1). Time-of-flight (TOF) transient-photocurrent technique measurements revealed a high μ_e of 2.0×10^{-3} cm² V⁻¹ s⁻¹ for **TPM-TAZ**, while the analogues of **TPM-TPB** and **TPM-i-**

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⁺ Electronic Supplementary Information (ESI) available: Detail single crystal X-ray diffraction data of TPM-TPB, TPM-TAZ and TPM-i-TAZ; TOF signal of the compounds.. See DOI: 10.1039/x0xx00000x

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TAZ achieved medium μ_{es} of 2.1 × 10⁻⁵ and 5.6 × 10⁻⁵ cm² V⁻¹ s⁻¹, respectively. X-ray diffraction analysis of the crystals shed light on the difference of their electron mobility. Using the three compounds as the ETMs, the blue phosphorescent OLEDs achieved good performance with a very low turn-on voltage of 2.4 V, a maximum current efficiency of 26.4 cd A⁻¹, and a maximum power efficiency of 26.9 lm W⁻¹.

Experimental section

General information

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All the reagents and solvents used for the synthesis or measurements were commercially available, and used as received unless otherwise stated.

The ¹H NMR and ¹³C NMR spectra were recorded on a MERCURY-VX300 spectrometer with CDCl₃, or CD₂Cl₂ as the solvent and tetramethylsilane as an internal reference. Molecular masses were determined by a VJ-ZAB-3F-Mass spectrometer. Elemental analyses were performed on a Vario EL-III microanalyzer. Single-crystal X-ray diffraction data of the samples were obtained from a Bruker AXS Smart CCD diffractometer by using a graphite-monochromated MoK α (λ = 0.71073 Å) radiation at 100 or 296 K. The data were collected using the $\omega/2\theta$ scan mode and corrected for lorentz and polarization effects as well as absorption during data reduction using Shelxtl 97 software. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on NETZSCH STA 449C instrument and NETZSCH DSC 200 PC unit under a nitrogen atmosphere. The thermal stability of the samples was determined by measuring their weight loss, heated at a rate of 10 °C min⁻¹ from room temperature to 800 °C. The glass transition temperature (T_g) was determined from the second heating scan at a heating rate of 10 °C min⁻¹ from -60 to 350 °C. Their UV-Vis absorption spectra were recorded on a Shimadzu UV-2500 recording spectrophotometer with baseline correction. Photoluminescence (PL) spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. Cyclic voltammetric studies of the compounds in reduction processes were carried out in nitrogen-purged dimethyl formamide (DMF) solution at room temperature with a CHI voltammetric analyzer. The conventional three-electrode configuration consists of a platinum working electrode, a platinum wire counter electrode, and a silver/silver chloride (Ag/Ag⁺) reference electrode. The Bu_4NPF_6 (0.1 M) was employed as the supporting electrolyte, and ferrocenium-ferrocene (Fc/Fc^{+}) was served as the internal standard. The lowest unoccupied molecular orbital (LUMO) energy levels (eV) of these compounds were calculated according to the formula: - $[4.8 \text{ eV} + (E_{\text{onset, reversible}} E_{1/2(\text{Fe/Fe}^+)}$]. The excitation light source used for TOF transientphotocurrent technique was a Nd:YAG laser (λ =355 nm, pulse width: 5 ns, Frequence: 10 Hz).

Device fabrication and characterization

The OLEDs were fabricated on the patterned 95-nm-thick indium tin oxide (ITO)-coated glass substrates with a sheet resistance of 15~20 Ω square⁻¹. Before device fabrication, the

ITO glass substrates were precleaned in sequence by ultrasonic bath of detergent, acetone, deionized water, and isopropyl alcohol, and then dried at 80 °C for more than 3 h. The devices were fabricated under a unbroken vacuum of $< 5 \times 10^{-4}$ Pa. 1,4,5,8,9,11-hexaazatriphenylene hexacarbonitrile (HATCN, 5 1,1-bis-(4-bis(4-methyl-phenyl)-amino-phenyl)nm). cyclohexane (TAPC, 30 nm), emitting layer [(Iridium(III)bis $(4,6-(difluorophenyl)pyridine-N,C^{2'})$ picolinate (Firpic): 2,6bis(3-(carbazol-9-yl)phenyl)pyridine (26DczPPy), 7 nm], electron transporting layer (TPM-TPB, TPM-TAZ or TPM-i-TAZ, 50 nm), LiF (1 nm), and finally A1 (80 nm) were deposited consecutively onto the ITO substrate. The light emissive area of the devices were 0.09 cm². The Current density-voltage-luminance (I-V-B) characteristics of the OLEDs were measured by Keithley source-measure unit 2400 and Konica Minolta chromameter CS-200. The electroluminescent (EL) spectra of the devices were measured by a spectrophotometer (Photo Research Model: SpectraScan PR-705). The external quantum efficiencies (EQEs) were calculated from the current densities, current efficiencies, and their corresponding EL spectra. All measurements were carried out at room temperature under ambient conditions.

Density functional theory (DFT) calculations

The geometrical and electronic properties of these pyrimidinecontaining star-shaped molecules were performed with the *Gaussian 09* program package.¹¹ The optimized calculation was obtained by means of the B3LYP-GD3 (Becke three parameters hybrid functional with Lee-Yang-Parr correlation functionals) with the 6-311G(d, p) atomic basis set.¹² Then the electronic structures were calculated at τ HCTHhyb/6-311++G(d, p) level.¹³ The triplet energy levels of the compounds were calculated at the same level of the theory using TDDFT method. Molecular orbitals were visualized using Gauss view 5.0.

Materials synthesis

3.5.6-tris(3-bromophenyl)-1.2.4-triazine (3): A mixture of 3bromobenzohydrazide (215 mg, 1 mmol),¹⁴ 1,2-bis(3bromophenyl)ethane-1,2-dione (368 mg, 1 mmol),¹⁵ ammonium acetate (231 mg, 3 mmol) and NaHSO₄/SiO₂ (200 mg) was thoroughly mixed in a mortar and then heated in the oil bath at 125 °C for 6h. The mixture was cooled down to room temperature and mixed thoroughly with 3 \times 20 ml of dichloromethane. The collected organic phase was washed with water and dried with anhydrous Na₂SO₄. After filteration and removal of the solvent, the residue was purified by column chromatography on silica gel (eluent: petroleum /dichloromethane = 1:1, v/v) to give the title compound as light yellow solid (338 mg, 62%). ¹H NMR (300 MHz, CD₂Cl₂) δ [ppm]: 8.78 (s, 1H), 8.59 (d, J = 7.8 Hz, 1H), 7.94 (s, 1H), 7.88 (s, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.62 (t, J = 7.5 Hz, 2H), 7.39-7.49 (m, 3H), 7.27 (d, J = 8.4 Hz, 1H), 7.22 (d, J = 8.1 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ [ppm]: 160.23, 154.39, 154.07, 137.06, 136.74, 136.22, 134.86, 134.17, 133.07, 132.67, 132.26, 131.25, 130.53, 130.15, 130.07, 128.54, 128.19, 127.03, 123.22, 123.02. MS (EI): m/z 546.74 [M⁺]. Anal. Calcd for

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 $C_{21}H_{12}Br_3N_3$: C 46.19, H 2.22, N 7.70. found: C 46.23, H 2.10, N 7.74.

1,3,5-tri(3-(pyrimidin-5-yl)phenyl)benzene (TPM-TPB): Pyrimidin-5-ylboronic acid (1.5 g, 11.8 mmol), 1,3,5-tri(3bromophenyl)benzene (1.3 g, 2.4 mmol), 16 Pd₂(dba)₃ (231 mg), and $[(t-Bu)_3P]HBF_4$ (316 mg) were added to a 25-mL Schlenk flask equipped with a stir bar in air. Dioxane (16 mL) and aqueous K₃PO₄ (1.27 M, 8 mL, 10.1 mmol) were added. The Schlenk flask was sealed and heated in an oil bath at 100 °C for 36 h with vigorous stirring. The mixture was then extracted with CH_2Cl_2 (3 \times 50 ml). The combined organic layer was washed with brine and then dried with anhydrous Na₂SO₄. The residue was then purified by column chromatography on silica gel (dichloromethane/methanol = 40:1, v/v) to give the title compound as white solid (1.3 g, yield: 95%). ¹H NMR (300 MHz, CDCl₃) δ [ppm]: 9.25 (s, 1H), 9.04 (s, 2H), 7.82-7.89 (m, 3H), 7.65-7.70 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ [ppm]: 164.58, 157.19, 142.12, 141.57, 138.06, 129.89, 129.07, 127.37, 127.26, 125.58, 119.22. MS (EI): m/z 540.38 [M⁺]. Anal. Calcd for C₃₆H₂₄N₆: C 79.98, H 4.47, N 15.55. found: C 80.39, H 4.53, N 15.36.

2,4,6-tris(3-(pyrimidin-5-yl)phenyl)-1,3,5-triazine (**TPM-TAZ**): The title compound was synthesized according to the similar procedure to **TPM-TPB**, with the participation of 2,4,6-tris(3-bromophenyl)-1,3,5-triazine^{10b} and using dichloromethane/methanol (v/v: 30:1) as eluant to give the title compound as white solid (yield: 55%). ¹H NMR (300 MHz, CDCl₃) δ [ppm]: 9.31 (s, 1H), 9.13 (s, 2H), 8.98 (s, 1H), 8.89 (d, J = 7.8 Hz, 1H), 8.87 (d, J = 7.8 Hz, 1H), 7.80 (t, J = 7.5 Hz 1H). ¹³C NMR (75 MHz, CDCl₃) δ [ppm]: 171.60, 158.08, 155.33, 137.22, 135.17, 134.16, 131.56, 130.32, 129.82, 127.63. MS (EI): m/z 543.09 [M⁺]. Anal. Calcd for C₃₃H₂₁N₉: C 72.92, H 3.89, N 23.19. found: C 73.05, H 3.92, N 23.06.

3,5,6-tris(3-(pyrimidin-5-yl)phenyl)-1,2,4-triazine (TPM-i-

TAZ): The title compound was synthesized according to the similar procedure to **TPM-TPB**, with the participation of intermediate **3**, and then purified by column chromatography on silica gel (dichloromethane/methanol = 30:1, v/v) to give the title compound as light yellow solid (yield 88%). ¹H NMR (300 MHz, CDCl₃) δ [ppm]: 9.28 (s, 1H), 9.23 (s, 2H), 9.11 (s, 2H), 8.95 (s, 1H), 8.86 (s, 2H), 8.80 (s, 4H), 7.95 (s, 1H), 7.76-7.91 (m, 6H), 7.50-7.62 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ [ppm]: 161.02, 157.89, 157.81, 157.77, 155.09, 154.98, 154.77, 136.55, 136.28, 135.48, 135.06, 135.00, 134.87, 133.74, 133.34, 133.18, 130.30, 130.13, 130.06, 130.00, 129.53, 128.84, 128.45, 128.36, 128.05, 126.76. MS (EI): m/z 543.26 [M⁺]. Anal. Calcd for C₃₃H₂₁N₉: C 72.92, H 3.89, N 23.19. found: C 72.96, H 3.99, N 23.05.

Results and discussion

Synthesis and characterization

The synthetic routes for the new pyrimidine-based electron transport materials were shown in Scheme 1. Target compounds of **TPM-TPB**, **TPM-TAZ** and **TPM-i-TAZ** were synthesized by Suzuki coupling reaction of pyrimidin-5ylboronic acid and the corresponding bromide precursors. The **TPM-TPB** and **TPM-i-TAZ** were obtained with high yield of 95% and 88% respectively, while **TPM-TAZ** was achieved with a medium yield of 55%. The three final products (**TPM-TPB**, **TPM-TAZ** and **TPM-i-TAZ**) were purified by column chromatography and subsequently sublimation, and the molecular structures were confirmed by ¹H NMR, ¹³C NMR and elemental analysis.



Scheme 1 Synthetic routes of the compounds.



Fig. 2 TGA and DSC traces (inset) of the three compounds.

Thermal properties

The thermal properties of the three compounds were investigated by TGA and DSC. The TGA measurement reveals their high thermal-decomposition temperatures (T_d , corresponding to 5% weight loss) of 420 °C for **TPM-TPB**, 400 °C for **TPM-TAZ** and 418 °C for **TPM-i-TAZ**, respectively (See Fig. 2 and Table 1). The DSC trace exhibits distinct glass-transition temperatures (T_g) of 112 °C for **TPM-TPB**, 131 °C for **TPM-TAZ** and 112 °C for **TPM-i-TAZ**, respectively (See the inset of Fig. 2). Compared with their analogue of TmPyPB, the thermostability is significantly improved by replacing the pyridine rings with pyrimidine rings.¹⁶

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Photophysical properties

Fig. 3 displays the UV-Vis absorption and fluorescence spectra of these compo in dichloromethane (DCM) solution, and e presented in Table 1. TPM-TPB, TPMthe detailed dat AZ show absorption peaks at 254, 293 and TAZ and TPM y, assigned to their π - π^* transitions.^{7a-c} In 296 nm, respec **FPM-TPB**, the absorption peaks of **TPM**contrast to that TAZ and TPM AZ display ca 40 nm red-shifts presumably due to the mor anar molecular structure, which could be resulted from intramolecular hydrogen bonds. Their fluorescence em on spectra exhibit peaks at 363 (TPM-TPB), 388 (TPM-TA and 389 nm (TPM-i-TAZ), respectively. Their triplet ene levels ($E_{\rm T}$ s) were estimated to be 2.83 eV for TPM-TPB, eV for TPM-TAZ and 2.43 eV for TPMi-TAZ, respecti from the highest-energy vibronic sub-band of the ph orescence spectra in frozen 2methyltetrahydr an matrix at 77 K (Fig. 3). Unexpectedly, i-TAZ owns a more twisted molecular despite the TI with the analogues of TPM-TPB and structure comp TPM-TAZ, the osphorescence spectra revealed a distinctly V, which could be elucidated from their lower $E_{\rm T}$ of 2. alculations discussed below. quantum chemic



Fig. 3 Normalized UV-Vis absorption and fluorescence emission spectrum of the compounds in dichloromethane solution, and phosphorescent emission in 2-methyltetrahydro furan at 77K.

Electrochemical properties

The electrochemical behaviors of the three compounds were determined by cyclic voltammetry (CV) using Fc/Fc^+ couple as the internal reference. As shown in Fig. 4, both the triazine cored compounds exhibit quasi-reversible reduction process in DMF solution, and the onset potentials are -1.95 V (*vs* Fc/Fc⁺) for **TPM-TAZ** and -1.82 V (*vs* Fc/Fc⁺) for **TPM-i-TAZ**, respectively. While unconspicuous reduction signal of **TPM-TPB** exhibits an onset potential of -1.99 V (*vs* Fc/Fc⁺). Their LUMO levels determined from the onset potentials of reduction are -2.81 eV (**TPM-TPB**), -2.85 eV (**TPM-TAZ**) and -2.98 eV (**TPM-i-TAZ**), respectively. Oxidation process were not observed for the three compounds, and thus their HOMO levels were deduced to be -7.04 eV for TPM-TPB, -6.67 eV for TPM-



Fig. 4 Reduction behaviors of the three compounds in CV.

Quantum chemical calculations

DFT calculations were performed to investigate the structureproperty relationship at the molecular level. As shown in Fig. 5, the LUMOs of TPM-TPB are distributed among the phenylpyrimidine arms, while TPM-TAZ and TPM-i-TAZ are mainly located at the central triazine core and the adjacent benzene rings, which can be understood from their stronger electronegativity of triazine core. The highest occupied molecular orbitals (HOMOs) of TPM-TPB are mainly located at the central 1,3,5-triphenylbenzene, whereas the HOMOs of TPM-TAZ are distributed in the peripheral phenylpyrimidine arms, which reveals a desirable separation of frontier molecular orbital (FMO). However, the HOMOs of TPM-i-TAZ are delocalized over the entire molecule which suggests a partial overlap of FMO, and thus induces a narrow energy bandgap (E_{σ}) and a low $E_{\rm T}$.¹⁷ Such results are consistent with the absorption and phosphorescent data as abovementioned. The calculated HOMO/LUMO values of the three compounds are -2.56/-7.00 eV for TPM-TPB, -2.59/-7.00 eV for TPM-TAZ and -2.70/-6.84 eV for TPM-i-TAZ, respectively, which are comparable to the measured values (Table 1).



Fig. 5 Calculated spatial distributions of the HOMO and LUMO levels of the compounds.

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compounds	absorption	bsorption emission E_{g}^{b} E_{T}^{c}		$E_{\rm T}^{\ \rm c}$	LUMO ^d /HOMO ^e	LUMO/HOMO ^f	$T_{\rm g}^{g}/T_{\rm m}^{g}/T_{\rm d}^{h}$
	λ_{\max}^{a} [nm]	λ_{\max}^{a} [nm]	[eŬ]	[eV]	[eV]	[eV]	[°C]
TPM-TPB	254	363	4.23	2.83	-2.81 /-7.04	-2.56 /-7.00	112 /247 /420
TPM-TAZ	293	388	3.82	2.82	-2.85 /-6.67	-2.59 /-7.00	131 /332 /400
TPM-i-TAZ	296	389	3.43	2.43	-2.98 /-6.41	-2.70 /-6.84	112 /250 /418

 Table 1. Thermal, photophysical, and electrochemical data of the materials.

^{*a*}Measured in dichloromethane. ^{*b*}Estimated from the optical absorption edges. ^{*c*}Estimated from the phosphorescent spectrum in 2methyltetrahydrofuran at 77 K. ^{*d*}Determined from the onset of reduction potentials. ^{*e*}Deduced from the LUMO and the optical energy gap. ^{*f*}Obtained from DFT calculations. ^{*g*}Obtained from DSC measurements. ^{*h*}Obtained from TGA measurements.

X-ray diffraction analysis

The single crystals of TPM-TPB and TPM-i-TAZ were readily obtained by sublimate recrystallization method, while that of TPM-i-TAZ was obtained by solvent diffusion method. The crystal structures of the compounds were determined by single crystal X-ray diffraction. As displayed in Fig. 6, both TPM-TPB and TPM-TAZ exhibit nearly a centrosymmetry structure. The dihedral angles of the central benzene ring and the adjacent arms of TPM-TPB are 39.0° (C1/C1A), 33.5° (C3/C3A) and 39.9° (C5/C5A), respectively (Fig. 6a), revealing a screwy molecular structure and less delocalized π -conjugation. In contrast, the dihedral angles of the central triazine ring and the adjacent arms of TPM-TAZ are 16.9° (C1/C1A), 4.0° (C2/C2A) and 10.6° (C3/C3A), respectively (Fig. 6b), implying an efficient π -extension. The molecular packing diagrams of TPM-TPB and TPM-TAZ are presented in Fig. 7. As demonstrated in Fig. 7a, the obtained C-H-N bond distances (2.88-3.61 Å) between pyrimidines and the adjacent molecules are reasonably classified as weak hydrogen bonds. For TPM-TAZ, the intramolecular C-H N hydrogen bonds exist between the central triazine ring and the adjacent phenyl rings, while the intermolecular hydrogen bonds exist between the peripheral pyrimidine rings and the adjacent molecules (Fig. 7b). The obtained intramolecular bond distances (2.45-2.55 Å) and

intermolecular bond distances (2.76-2.94 Å) indicate that these hydrogen bonds are as short as covalent bonds.



Fig. 6 X-ray structure of TPM-TPB (a) and TPM-TAZ (b) *via* sublimate recrystallization method.

The X-ray structure of **TPM-i-TAZ** is displayed in Fig. 8a and their molecular packing diagram is presented in Fig. 8b. The dihedral angles of the central triazine ring and the adjacent arms of **TPM-i-TAZ** are 48.7° (C1/C1A), 37.7° (C2/C2A) and 11.4° (C3/C3A), respectively. The obtained C-H^{...}N bond distances of **TPM-i-TAZ** vary from 2.47 to 2.76 Å (Fig. 8b), which can be classified as moderate intensity hydrogen bonds in between **TPM-TPB** and **TPM-TAZ**.



Fig. 7 Molecular packing diagrams of TPM-TPB (a) and TPM-TAZ (b).





Fig. 8 X-ray structure of TPM-i-TAZ via solvent diffusion method (a), and their molecular packing diagram (b).

Carrier-transport properties

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The carrier mobilities of the three compounds in amorphous thin film were characterized by the TOF transient-photocurrent technique.¹⁸ The configuration of the devices were ITO/Alq₃ (20 nm)/**TPM-TPB** (944 nm), **TPM-TAZ** (943 nm) or **TPM-i-TAZ** (1260 nm)/Al. The carrier mobility (μ) was calculated according to the following formula: $\mu = D/(ET_t) = D^2/(VT_t)$, where T_t is the charge transit time, V is the applied bias, D is the thickness of organic layer.



Fig. 9 Electron mobilities of the compounds under different electric field intensity.

Fig. 9 shows the electron mobilities of these compounds plotted as a function of the sequare root of the electric field. The electron mobilities of **TPM-TPB** lies in the range of 1.7×10^{-5} to 2.1×10^{-5} cm² V⁻¹ s⁻¹ at electric field between 4.1×10^{5} V cm⁻¹ and 8.3×10^{5} V cm⁻¹. As expected, **TPM-TAZ** shows a higher electron mobilities ranging from 1.2×10^{-3} to 2.0×10^{-3} cm² V⁻¹ s⁻¹ at electric field between 2.1×10^{5} V cm⁻¹ and 4.2×10^{5} V cm⁻¹. While the electron mobilities of TPM-i-TAZ are between TPM-TPB and TPM-TAZ, with μ_{e} range from 4.9×10^{-5} to 5.6×10^{-5} cm² V⁻¹ s⁻¹ at electric field between 3.1×10^{5} V cm⁻¹ and 7.0×10^{5} V cm⁻¹. The measured μ_{e} s of the compounds correlate well with our X-ray diffraction analysis. The favorable intramolecular and intermolecular hydrogen bonds result in planar molecular structure and more delocalized π -conjugation (Fig. 7 and Fig. 8b), and then induce an easier electron hopping between the adjacent molecules.¹⁹ To the best of our knowledge, the μ_e of TPM-TAZ is the highest among the ETMs with high triplet energy (Table 2).

Table 2. The electron mobilities comparison of high $E_{\rm T}$ ETMs.

ETMs	$E_{\rm T} [{\rm eV}]$	$\mu_{\rm e} [{\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1}]$	$E [V cm^{-1}]$	Ref.
TPM-TPB	2.83	2.1×10^{-5}	7.3×10^{5}	this work
TPM-TAZ	2.82	2.0×10^{-3}	$3.1 imes 10^5$	this work
TmPyPB	2.75	1.0×10^{-3}	$6.4 imes 10^5$	16
pTPOTZ	2.95	$3.4 imes 10^{-4}$		20
3TPYMB	2.98	$\sim 10^{-5}$		21
SiTAZ	2.84	6.2×10^{-4}		22

Performance of OLEDs

Firpic-based blue OLEDs were fabricated to evaluate the property of the three compounds as ETMs. The phosphorescent OLEDs were fabricated with the following device configuration: ITO (95 nm)/HATCN (5 nm)/TAPC (30 nm)/Firpic (12 wt %): 26DCzPPy (7 nm)/ETMs (50 nm)/LiF (1 nm)/Al (80 nm), where HATCN and LiF served as the hole- and electron-injecting layers, respectively, TAPC was employed as the hole-transporting materials, 26DCzPPy was used as the host material, and Firpic was used as the blue phosphor. **TPM-TAZ**, **TPM-TAZ** and **TPM-i-TAZ** were employed as the ETMs in device A, B and C, respectively. The current density-voltage-brightness (*I-V-B*) characteristics, EL spectra and the efficiencies as functions of the current density for all these devices are shown in Fig. 10, and their performances are summerized in Table 3.

As revealed in Fig. 10 and Table 3, device A and B show comparable EL efficiencies. A maximum current efficiency ($\eta_{c, max}$) of 26.4 cd A⁻¹, a maximum power efficiency ($\eta_{p, max}$) of 24.0 lm W⁻¹ and a maximum external quantum efficiency ($\eta_{ext, max}$) of 12.1% were achieved for device A, while an $\eta_{c, max}$ of 24.0 cd A⁻¹, an $\eta_{p, max}$ of 26.9 lm W⁻¹ and an $\eta_{ext, max}$ of 10.1% were achieved for device B. Noticeably, the efficiencies of Published on 14 January 2016. Downloaded by University of California - San Diego on 14/01/2016 20:10:06

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Table 3. Comparison of the EL performances of device A, B and C.

Device	ETM	$V_{on}^{\ a}$ [V]	$\frac{L_{\max}^{b} [cd m^{-2}]}{(V at L_{\max}, V)}$	Max. Efficiency			Luminance at 1000 cd m ⁻²			
				$\eta_{c, max}^{c}$	$\eta_{p, max}^{d}$	$\eta_{ext, max}^{e}$	V	η_c	η_p	η_{ext}
				$\left[cd A^{-1} \right]$	$[\text{Im } W^{-1}]$	[%]		$\left[cd A^{-1} \right]$	$[\text{Im W}^{-1}]$	[%]
А	TPM-TPB	3.7	12784 (13.6)	26.4	24.0	12.1	7.8	20.8	8.3	9.4
В	TPM-TAZ	2.4	11701 (8.4)	24.0	26.9	10.1	3.2	18.9	18.4	7.9
С	TPM-i-TAZ	3.5	189 (10.8)	0.14	0.16	0.06				

^{*a*}Turn-on voltage at 1 cd m⁻²; ^{*b*}L_{max}: maximum luminance; ^{*c*} $\eta_{c, max}$: maximum current efficiency; ^{*d*} $\eta_{p, max}$: maximum power efficiency; ^{*e*} $\eta_{ext, max}$: maximum external quantum efficiency.



Fig. 10 (a) *I-V-B* characteristics; (b) current efficiency and power efficiency, and (c) external quantum efficiency (EQE) versus current density; (d) EL spectra at 1 mA cm⁻² of the devices.

device A and B showed slightly roll-off over a wide range of luminance, and high efficiencies are maintained even at high luminance of 1000 cd m⁻². In contrast, the poor performances of device C can be ascribed to the low $E_{\rm T}$ of the ETMs, which lead to undesirable exciton diffusion from the emission layer to the electron transporting layer since the emission from the ETL of TPM-i-TAZ can be clearly observed (Fig. 10d and Fig. S4).

It is noteworthy that, device B achieved an extremely low turn-on voltage of 2.4 V (Fig 10a), which can be attributed to the favorable ETM of TPM-TAZ that has both favorable electron injection energy levels (LUMO = -2.85 eV) and high μ_e (2.0 × 10⁻³ cm² V⁻¹ s⁻¹).²³ Moreover, the low driving voltage of device B results in a high power efficiency of 26.9 lm W⁻¹. Considering the high μ_e and high E_T of TPM-TAZ, we believe that the EL performance could be further enhanced by

optimizing the device configurations and the fabrication process.

Conclusion

In summary, three new star-shaped compounds with different central cores and pyrimidine as the periphery are designed and synthesized. By fine-tuning the molecular structure and rationally utilizing the intramolecular/intermolecular hydrogen bonds, the desirable ETMs with both high $E_{\rm T}$ and high $\mu_{\rm e}$ have achieved. Eventually, a desirable ETM of **TPM-TAZ** is achieved, with a high $\mu_{\rm e}$ of 2.0×10^{-3} cm² V⁻¹ s⁻¹ that is nearly independent on the electric field, a high $E_{\rm T}$ of 2.82 eV and a high $T_{\rm g}$ of 131 °C. Using these compounds as ETMs, the blue phosphorescent OLEDs show an extremely low turn-on voltage

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of 2.4 V, a maximum current efficiency up to 26.4 cd A^{-1} , and a maximum power efficiency up to 26.9 lm W^{-1} .

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New pyrimidine-containing triazine-cored compound with high $E_{\rm T}$ and high $\mu_{\rm e}$ was synthesized. Using it as ETLs, the Firpic-based PhOLEDs achieved a low turn-on voltage of 2.4 V and high efficiencies.