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Triazole-Phosphine Oxide Electron Transporter for Ultralow-Voltage-Driven Sky Blue PHOLEDs

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1,3,5-Triazole derivatives **xTPOTZ** with aryl phosphine oxide (APO) groups at ortho-, meta- and parapositions were designed and prepared to demonstrate an APO modification strategy for developing n-type semiconductors. Optical analysis showed that the involvement of APO groups can hardly alter excited 10 state characteristics of **xTPOTZ**, rendering their triplet energy beyond 2.95 eV for effective exciton blocking in sky blue phosphorescent organic light-emitting diodes. The strong electron-withdrawing effect of P=O can effectively enhance electroactivity of the materials, on the basis of suitable substitution configuration. **mTPOTZ** and **pTPOTZ** with the low-lying lowest unoccupied molecular orbitals at ~-3.4 eV show the improved electron affinity, as well as the reduced highest occupied molecular orbital at -6.6 is eV for effective hole blocking. The estimated electron mobility of *m*TPOTZ and *p*TPOTZ reaches to the order of 10⁻⁴ cm² V⁻¹ s⁻¹. Furthermore, owing to the strongest intramolecular interactions and the exposed triazole core under para-substitution configuration, pTPOTZ achieves the lowest LUMO at -3.46 eV and the highest μ_e of 3.4×10^{-4} cm² V⁻¹ s⁻¹, which is among the highest values reported so far for high-energygap electron-transporting materials (ETM). As the result, *p***TPOTZ** endowed its typical *m*CP and FIrpic-²⁰ based sky blue PHOLEDs with the ultralow onset voltage of 2.5 V and favourable external quantum efficiency up to ~20%, revealing the effectiveness of APO modification for high-performance ETM development.

1. Introduction

- Electrophosphorescence is believed as one of the most promising ²⁵ technologies competent for the environmentally friendly flatpanel displays and lightings with the advantage of simultaneously utilizing singlet and triplet excitons.¹⁻⁸ Since exciton is formed through hole and electron recombination, balanced carrier injection and transportation is one of the core concerns for ³⁰ achieving high-efficiency phosphorescent light-emitting diodes (PHOLEDs).⁹⁻¹⁰ However, as conjugated systems with delocalized π electrons, most of organic semiconductors prefer to transport hole rather than electron, causing unbalanced charge flux in their devices.¹¹ Actually, hole mobility ($\mu_{\rm h}$) of common
- ³⁵ hole transporting materials, such as di-[4- 1,1-bis](di-4-tolylamino)phenyl]cyclohexane (TAPC, 10⁻² cm² V⁻¹ s⁻¹)¹² and 4,4'-bis[N-(p-tolyl)-N-phenyl-amino]biphenyl (TPD, 10⁻³ cm² V⁻¹ s⁻¹)¹³, is one to four orders of magnitude larger than electron mobility (µ_e) of conventional electron transporting materials ⁴⁰ (ETM), e.g. 1,3,5-tris(*N*-phenylbenzimidizol-2-yl)benzene (TPBI, 10⁻⁶ cm² V⁻¹ s⁻¹)¹⁴, 4,7-diphenyl-1,10-phenanthroline (Bphen, 10⁻⁴ cm² V⁻¹ s⁻¹)¹⁵ and 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB, 10⁻⁴ cm² V⁻¹ s⁻¹)¹⁶, making exciton recombination zone shift to interfaces between emissive layers (EML) and

For blue PHOLEDs, the first triplet energy level (T₁) of ETM should be over 2.8 eV to suppress triplet exciton diffusion, rendering the employment of $meso^{14, 20}$ or twisted²¹ linkages. In 55 contrast, high μ_e requires planar configurations with extended conjugations and strong intermolecular interactions for facile charge hopping. This reflects the intrinsic contradiction between optical and electrical properties of high-energy-gap ETMs. Accordingly, nitrogen-bearing heterocycles seem superior as 60 building blocks for ETMs with large electron affinity, planar configuration and high triplet energy. Represented by TmPyPB¹⁶ pyridine²²⁻²⁴, pyrimidine²⁵ and 1,3,5-triazole²⁶ have been adopted to construct high-energy-gap ETMs for blue PHOLEDs. Low driving voltages, such as 3.0 V for onset, and high efficiencies, 65 e.g. external quantum efficiency (EQE) more than 10% were already realized through conventional device configurations. Nevertheless, it is noteworthy that although meso linkage is utilized during system extension, triplet energy of these ETMs is

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⁴⁵ electron transporting layers (ETL)¹⁵. In this case, ETM should have triplet energy higher than those of phosphors to block triplet exciton diffusion and the highest occupied molecular orbital deeper than those of EML materials to restrain hole leakage.¹⁷ Therefore, in common sense, ETM development is focused on ⁵⁰ improving μ_e , triplet energy and electron injecting/hole blocking ability.¹⁸⁻¹⁹

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still around 2.8 eV, which should be elevated for efficient suppression of exciton diffusion.



Fig. 1 Chemical structures of xTPOTZ (x = o, m or p) (a) and single-crystal structures of oTPOTZ (b) and mTPOTZ (c).

In recent years, aryl phosphine oxide (APO) group is of great concern as a unique electroactive insulating linkage.²⁷⁻²⁹ Its strong electron-withdrawing inductive effect can polarize molecules and enhance electron affinity, while σ_{C-P} bond can ¹⁰ effectively block intramolecular electronic communications to restrain influences of functionalization on triplet energy.³⁰⁻³⁶ In this sense, APO group is ideal for constructing high-energy-gap ETMs. After primary attempts to improve electron injection and transportation with ETMs of triphenylphosphine oxide (TPPO)³⁷ and its pyrenyl³⁸ and spiro-fluorenyl derivatives³⁹, *m*-terphenyl⁴⁰-

⁴¹ and tetraphenylsilicanyl⁴² are modified by diphenylphosphine oxide (DPPO) on account of high triplet energy for applications in sky blue PHOLEDs. Although high efficiencies were realized due to the effective exciton confinement in EMLs, the weak

20 electron affinity of *m*-terphenyl and tetraphenylsilicanyl gave rise to the big driving voltages and low luminance of the devices. Regarding to this case, it is rational and imperative to develop feasible strategies to combine nitrogen-bearing heterocyclic skeletons and APO groups for the integration of their respective 25 superiorities in electrical performance and triplet energy

preservation.

In this contribution, a series of 1,3,5-triazole and TPPO hybrids, collectively named **xTPOTZ** (x = o, m and p,

corresponding to the substitution positions on TPPO groups), 30 were designed and prepared (Fig. 1a). Compared to parent molecule 2,4,6-triphenyl-1,3,5-triazine (TPTZ), the involvement of APO groups in xTPOTZ remarkably improves their thermal stability during operation, including the temperatures of decomposition (T_d) over 400 °C and melting points (T_m) more 35 than 250 °C. Meanwhile, by virtue of insulating characteristics of PO linkage, xTPOTZ completely inherit optical properties of TPTZ. Their triplet energy beyond 2.95 eV makes them competent as high-energy-gap ETM for sky blue PHOLEDs with bis(4,6-(difluorophenyl)pyridinato- N,C^2)picolinate iridium(III) ⁴⁰ (FIrpic, $T_1 = 2.65 \text{ eV}$) as phosphor. According to density function theory (DFT) calculation, although DPPO groups are only involved in their highest occupied molecular oribtals (HOMO), both of the HOMOs and the lowest unoccupied molecular orbitals (LUMO) of *m*TPOTZ and *p*TPOTZ remarkably descend, 45 indicating the enhanced electron injecting/hole blocking ability by the strong electron-withdrawing effect of P=O. This is consistent with cyclic voltammetric (CV) analysis results that due to its twisted configuration, oTPOTZ shows the HOMO and LUMO energy levels identical with those of TPTZ, while the 50 frontier molecular orbital (FMO) energy levels of mTPOTZ and *p***TPOTZ** are reduced for more than 0.12 eV, respectively.

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Estimated by I-V characteristics of the nominal electron-only devices, *p***TPOTZ** achieves the μ_e of 3.4×10⁻⁴ cm² V⁻¹ s⁻¹, which is among the highest values reported so far for high-energy-gap ETMs.⁴³ To manifest the advantage of *x*TPOTZ as ETMs, their 5 FIrpic-based sky blue PHOLEDs with a common host 1,3bis(9H-carbazol-9-yl)benzene (mCP) were fabricated without any structural optimization. Compared to the four-layer device of commercially available TmPyPB⁴⁴, pTPOTZ endowed its trilayer device with the dramatically reduced driving voltages of

 $_{10}$ 2.6 V for onset and 4.0 V at 100 cd m⁻² and the comparable EQE with maximum of ~13%, convincingly reflecting the great

potential of APO-substituted heterocycles n-type as semiconductors for various optoelectronic applications. w Article Online

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2. Experimental Section

15 2.1 Materials and Instruments

All the reagents and solvents used for the synthesis of the compounds were purchased from Aldrich and Acros companies and used without further purification.



XTBTZ

Scheme 1 Synthetic procedure of *x*TPOTZ (x = o, m or p).

¹H, ¹³C and DEPT135° NMR spectra were recorded using a Varian Mercury plus 400NB spectrometer relative to tetramethylsilane (TMS) as internal standard. Molecular masses were determined by a Bruker microflex MALDI-TOF Mass 25 Spectrometry. Elemental analyses were performed on a Vario EL III elemental analyzer. The crystal suitable for single-crystal XRD analysis was obtained by diffusion method at room temperature. All diffraction data were collected at 295 K on a diffractometer graphite Rigaku Xcalibur Е with ³⁰ monochromatized Mo K α ($\lambda = 0.71073$ Å) radiation in ω scan mode. All structures were solved by direct method and difference Fourier syntheses. Non-hydrogen atoms were refined by fullmatrix least-squares techniques on F2 with anisotropic thermal

- parameters. The hydrogen atoms attached to carbons were placed 35 in calculated positions with C-H = 0.93 Å and U(H) = 1.2Ueq(C)in the riding model approximation. All calculations were carried with the SHELXL97 program. Absorption out and photoluminescence (PL) emission spectra of the target compound were measured using a SHIMADZU UV-3150 spectrophotometer
- 40 and a SHIMADZU RF-5301PC spectrophotometer, respectively. The molar extinction coefficient (ε) was estimated according to the Lambert-Beer's Law as $\varepsilon = A/C \cdot L$, where A is absorbence, C is molar concentration in mol L^{-1} and L is optical distance in cm. Thermogravimetric analysis (TGA) and differential scanning
- 45 calorimetry (DSC) were performed on Shimadzu DSC-60A and DTG-60A thermal analyzers under nitrogen atmosphere at a heating rate of 10 °C min-1. Cyclic voltammetric (CV) studies were conducted using an Eco Chemie B. V. AUTOLAB potentiostat in a typical three-electrode cell with a platinum sheet
- 50 working electrode, a platinum wire counter electrode, and a silver/silver nitrate (Ag/Ag^{T}) reference electrode. A11 electrochemical experiments were carried out under a nitrogen atmosphere at room temperature in dichloromethane.

Phosphorescence spectra were measured in dichloromethane 55 using an Edinburgh FPLS 920 fluorescence spectrophotometer at 77 K cooling by liquid nitrogen with a delay of 300 μ s using Time-Correlated Single Photon Counting (TCSPC) method with a microsecond pulsed Xenon light source for 0.1 μ s-10 s lifetime measurement, the synchronization photomultiplier for signal 60 collection and the Multi-Channel Scaling Mode of the PCS900 fast counter PC plug-in card for data processing.

2.2 Synthesis

afford the bromides.

2.2.1 General synthetic procedure of 2,4,6-tri(bromophenyl)-1,3,5-triazine

65 In Ar₂, bromobenzonitrile (4.55 g, 25 mmol) in anhydrous added chloroform (150 mL) was dropwise to trifluoromethanesulfonic acid (7.50 g, 50 mmol) at 0 °C. The resulted mixture was warmed to room temperature and stirred for 24 h. Then, water (250 mL) was added. After a further stir for 2 h. ⁷⁰ the precipitate was filtrated and washed with water (3 \times 10 ml) and cold chloroform $(3 \times 10 \text{ ml})$, which was then dried in air to

2,4,6-Tri(2-bromophenyl)-1,3,5-triazine (oTBTZ): 2.74 g of white powder with a yield of 60%. ¹H NMR (TMS, CDCl₃, 400 75 MHz): $\delta = 8.118-8.096$ (dd, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz, 3H), 7.762 (d, J = 8.0 Hz,3 H), 7.506-7.469 (t, J = 7.6 Hz,3 H), 7.392-7.350 ppm (td, J₁ = 8.0 Hz, J₂ = 1.2 Hz, 3 H); LDI-TOF: m/z (%): 545 (100) $[M^+]$, 547 (100) $[M+2^+]$; elemental analysis (%) for $C_{21}H_{12}Br_3N_3$: C 46.19, H 2.22, N 7.70; found: C 46.21, H 2.23, N 80 7.75.

2,4,6-Tri(3-bromophenyl)-1,3,5-triazine (mTBTZ): 2.97 g of white powder with a yield of 65%. ¹H NMR (TMS, CDCl₃, 400 MHz): $\delta = 8.838$ (s, 3 H), 8.672 (d, J = 8.0 Hz,3 H), 7.757 (d, J =8.0 Hz,3 H), 7.485-7.445 ppm (t, J = 8.0 Hz,3 H); LDI-TOF: m/z 85 (%): 545 (100) [M⁺], 547 (100) [M+2⁺]; elemental analysis (%) for C₂₁H₁₂Br₃N₃: C 46.19, H 2.22, N 7.70; found: C 46.23, H 2.25,

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2,4,6-*Tri*(4-bromophenyl)-1,3,5-triazine (**pTBTZ**): 3.20 g of white powder with a yield of 70%. ¹H NMR (TMS, CDCl₃, 400 MHz): $\delta = 8.606$ (d, J = 8.8 Hz, 6H), 7.713 ppm (d, J = 8.8Hz,

⁵ 6H); LDI-TOF: m/z (%): 545 (100) [M⁺], 547 (100) [M+2⁺]; elemental analysis (%) for C₂₁H₁₂Br₃N₃: C 46.19, H 2.22, N 7.70; found: C 46.20, H 2.22, N 7.72.

2.2.2 General procedure for the palladium-catalyzed phosphorylation

- ¹⁰ In Ar₂, 2,4,6-tri(bromophenyl)-1,3,5-triazine (0.546 g, 1 mmol), NaOAc (0.27 g, 3.3 mmol), Pd(OAc)₂ (6.7 mg, 0.03 mmol), diphenylphosphine (0.6 mL, 3.3 mmol) was dissolved in N,Ndimethylformamide (5 mL). The mixture was heated to 130 °C and then stirred for 24 h. After cooled to room temperature, the
- ¹⁵ mixture was poured into water (50 mL) and extracted with CH_2Cl_2 (3 × 10 ml). The combined organic phase were dried with anhydrous Na_2SO_4 and concentrated in *vacuo*. The resident was further purified by flash column chromatography (5:1 EtOAc/EtOH).
- 2,4,6-Tris(2-(diphenylphosphoryl)phenyl)-1,3,5-triazine

(*oTPOTZ*): 0.64 g of white powder with a yield of 70%. ¹H NMR (TMS, DMSO, 400 MHz): $\delta = 7.770-7.743$ (m, 3H), 7.601-7.523 (m, 6H), 7.492-7.458 (m, 6H), 7.371-7.256 ppm (m, 27H); ¹³C NMR (TMS, DMSO, 100 MHz): $\delta = 170.932$ (C), 140.193(C),

- ²⁵ 135.365(CH, observed from DEPT135°), 134.817(C), 133.752(C), 133.573(CH), 131.900(CH), 131.574(CH), 131.116(CH), 130.109(CH), 128.106(CH) ppm; LDI-TOF.m/7(0), View Article Online [M⁺]; FTIR (KBr pellet): 3053, 1589 (C=N stretching), 1567 (C=C stretching), 1517, 1483, 1436, 1359, 1196 (P=O stretching),
- ³⁰ 1117, 1070, 844, 748, 717, 698, 545, 516 cm⁻¹; elemental analysis
 (%) for C₅₇H₄₂N₃O₃P₃: C 75.24, H 4.65, N 4.62, O 5.28; found: C 75.26, H 4.68, N 4.77, O 5.35.

2,4,6-Tris(3-(diphenylphosphoryl)phenyl)-1,3,5-triazine

- (*mTPOTZ*): 0.54 g of white crystal with a yield of 60%. ¹H NMR ³⁵ (TMS, CDCl₃, 400 MHz): δ = 8.981 (d, *J* = 8.4 Hz,,3H), 8.744-8.721 (dd, *J_I* = 8.0 Hz, *J₂* = 1.2 Hz, 3H), 7.917-7.869 (m, 3H), 7.750-7.699 (m, 12H), 7.670-7.625 (td, *J_I* = 7.6 Hz, *J₂* = 2.8 Hz, 3H), 7.581-7.482 ppm (m, 18H); ¹³C NMR (TMS, DMSO, 100 MHz): δ = 170.924(C), 136.183(CH), 135.987(C), 133.877(C),
- ⁴⁰ 132.847(CH), 132.554(CH), 132.207(CH), 132.110(CH), 131.683(C), 129.113(CH), 128.766(CH) ppm; LDI-TOF: m/z (%): 909 (100) [M⁺]; FTIR (KBr pellet): 3052, 1594 (C=N stretching), 1580 (C=C stretching), 1520, 1483, 1436, 1357, 1200 (P=O stretching), 1116, 721, 694, 641, 544 cm⁻¹; elemental analysis (%) ⁴⁵ for $C_{57}H_{42}N_3O_3P_3$: C 75.24, H 4.65, N 4.62, O 5.28; found: C
- ⁴⁵ for $C_{57}H_{42}N_3O_3P_3$; C /5.24, H 4.65, N 4.62, O 5.28; found: C 75.29, H 4.66, N 4.71, O 5.37.



Fig. 2 Single-crystal packing diagram of oTPOTZ and mTPOTZ.

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2,4,6-Tris(4-(diphenylphosphoryl)phenyl)-1,3,5-triazine (*pTPOTZ*): 0.50 g of white powder with a yield of 55%. ¹H NMR (TMS, CDCl₃, 400 MHz): $\delta = 8.824-8.797$ (dd, $J_1 = 8.4$ Hz, J₂ = 2.4 Hz, 6H), 7.921-7.872 (d, J = 11.6 Hz,, 6H), 7.740-7.689 s (m, 12H), 7.599-7.559 (t,d, J₁ = 7.6 Hz, J₂ = 1.2 Hz, 6H),7.515-7.471 ppm (t,d, J_1 = 7.6 Hz, J_2 = 2.4 Hz,12H); ¹³C NMR (TMS, DMSO, 100 MHz): $\delta = 171.291(C)$, 138.767(C), 137.900(C), 132.579(CH), 132.260(CH), 136.893(C), 132.122(CH). 128.919(CH), 128.752(CH) ppm; LDI-TOF: m/z (%): 909 (100) ¹⁰ [M⁺]; FTIR (KBr pellet): 3053, 1572, 1516, 1436, 1356, 1198, 1114, 808, 728, 714, 694, 558, 546 cm⁻¹; elemental analysis (%) for C₅₇H₄₂N₃O₃P₃: C 75.24, H 4.65, N 4.62, O 5.28; found: C 75.27, H 4.64, N 4.68, O 5.33.

2.3 Density function theory (DFT) Calculations

¹⁵ DFT computations were carried out with different parameters for structure optimizations and vibration analyses. The ground states and triplet states of molecules in vacuum were optimized by the restricted and unrestricted formalism of Beck's three-parameter hybrid exchange functional⁴⁵ and Lee, and Yang and Parr ²⁰ correlation functional⁴⁶ (B3LYP)/ 6-31G(d) respectively. The ground-state configurations of *o*-**TPOTZ** and *m*-**TPOTZ** were generated according to single crystal data. The fully optimized stationary points were further characterized by harmonic vibrational frequency analysis to ensure that real local minima ²⁵ had been found without imaginary vibrational frequency. The total energies were also corrected by zero-point energy both for the ground state and triplet state. The spin density distributions were visualized with Gaussview 3.0. All computations were performed using the Gaussian 03 package.⁴⁷

30 2.4 Device Fabrication and Testing

Before loading into a deposition chamber, the ITO substrate was cleaned with detergents and deionized water, dried in an oven at 120 °C for 4 h, and treated with UV-ozone for 20 min. Devices were fabricated by evaporating organic layers at a rate of 0.1-0.3 35 nm s⁻¹ onto the ITO substrate sequentially at a pressure below

- 1×10^{-6} mbar. Onto the TPBI layer, a layer of LiF with 1 nm thickness was deposited at a rate of 0.1 nm s⁻¹ to improve electron injection. Finally, a 100-nm-thick layer of Al was deposited at a rate of 0.6 nm s⁻¹ as the cathode. The emission area of the devices 40 was 0.14 cm² as determined by the overlap area of the anode and
- ⁴⁰ was 0.14 cm as determined by the overlap area of the anode and the cathode. The EL spectra and CIE coordinates were measured using a PR650 spectra colorimeter. The current-density-voltage and brightness–voltage curves of the devices were measured using a Keithley 2400/2000 source meter and a calibrated silicon
- ⁴⁵ photodiode. All the experiments and measurements were carried out at room temperature under ambient conditions.

3. Results and Discussions

3.1 Design and Synthesis

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1,3,5-Triazole is an extremely electron-deficient ring with high 50 electron affinity. Even directly substituted with electron-donating groups, such as carbazole and diphenylamine, its derivatives still exhibit favorable electron injecting/transporting ability.^{26, 48} Su et al. showed that electron affinity of 2,4,6-tri(biphenyl-3-yl)-1,3,5triazine is as high as 3.0 eV, which can be further increased to 3.3 55 eV by incorporating peripheral pyridine groups.⁴⁹ However, triplet energy of these meso-linked materials remains too low as 2.7-2.8 eV to afford the positive energy transfer to FIrpic, indicating T_1 energy of **TPTZ** core highly sensitive to conjugation extension and substitution with electron-withdrawing 60 groups. Meanwhile, we and other groups have demonstrated that the introduction of APO group in conjugated systems can polarize molecules, accompanied with negligible T₁ variation less than 0.1 eV. Therefore, it is rational to utilize DPPO as the secondary electron-withdrawing group with superiority in carrier 65 injection enhancement and triplet energy preservation. Furthermore, through making use of its big steric hindrance, various substitution positions of DPPO group in xTPOTZ can modulate the planarity and conjugation of TPTZ core and adjust the intermolecular interactions, thereby establishing a flexible 70 platform to investigate the correlations between molecular configuration of ETMs and their optoelectronic properties. From another point of view, xTPOTZ are actually combinations of two conventional high-energy-gap electron-deficient units, namely TPPO and 1,3,5-triazole, through ortho-, meta- and para-linkages, 75 respectively, with different inter-group interplays (Fig. 1a), which would testify the optimal linkage style to integrate superiorities of TPPO and 1,3,5-triazole to the greatest extent.

*x***TPOTZ** were conveniently prepared from bromobenzonitrile through cyclization and phosphorylation with moderate overall 80 yields of ~40%, respectively (Scheme 1). Their chemical structures were characterized and certified on the basis of mass spectrometry, NMR spectroscopy and elemental analysis. The molecular configurations and intermolecular interactions of oTPOTZ and mTPOTZ were further confirmed by X-ray 85 diffraction of their single crystals (Fig. 1b, 1c and 2). The mesasubstitution configuration of mTPOTZ renders its almost planar TPTZ core with small dihedral angles between three phenyls and triazole of $6.77(1)^\circ$, $12.73(6)^\circ$ and $13.68(4)^\circ$, respectively; while dihedral angles of TPTZ core in oTPOTZ are remarkable larger ⁹⁰ as 28.05(0)°, 43.11(5)° and 54.20(8)°, respectively, verifying the twisted configuration and reduced conjugation of oTPOTZ due to its ortho-linked DPPOs. Close inspection on packing diagrams reveals one-dimensional chains of oTPOTZ and mTPOTZ. P=O ... H and edge-to-centroid distances between DPPO and 95 TPTZ groups are 2.892(9) and 3.757(9) Å for oTPOTZ and 3.324(8) and 3.288(6) Å for mTPOTZ, indicating weak hydrogen bond and π - π stacking interactions between adjacent molecules. Obviously, the interactions between peripheral DPPOs and TPTZ cores establish the effective channels for 100 intermolecular electron transport. Although single crystal of

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*p***TPOTZ** was not obtained, it is convincible that its *para*substituted and protrudent DPPO groups would result in the planar **TPTZ** core and considerable intermolecual DPPO-**TPTZ** interactions. In this sense, *m***TPOTZ** and *p***TPOTZ** with s extended conjugations and planar configurations would be superior to *o***TPOTZ** in electron transportation.

3.2 Thermal Stability

Thermal performance is significant for ETMs, which would influence stability of their thin films during device operation. 10 Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of xTPOTZ and TPTZ were measured to Fig. out the contribution of APO groups to thermal property improvement (Fig. 3 and Table 1). It is convincing that no matter of substitution position, the involvement of steric DPPO groups 15 in xTPOTZ should decrease the intermolecular interactions between their TPTZ cores. However, even for nonplanar *o***TPOTZ**, its melting point (T_m) of 273 °C is 40 °C bigger than that of TPTZ, revealing DPPO-induced stronger intermolecular interactions, namely P=O \cdots H hydrogen bonds and π - π 20 interactions between DPPO and TPTZ core as shown by single crystal result. It is noteworthy that the melting points of oTPOTZ and *m***TPOTZ** are comparable, but T_m of *p***TPOTZ** is improved to 320 °C with a further increase of ~40 °C, which rationally manifests its strongest intermolecular interactions in xTPOTZ.

²⁵ TGA curves show that the decomposition temperatures (T_d) of **xTPOTZ** at weight loss of 5% are more than 420 °C, which are dramatically improved for more than 170 °C in comparison to that of **TPTZ**. The residues in crucibles after heating evidence the decomposition of these compounds under heating rather than ³⁰ sublimation or volatilization. Furthermore, on the basis of the same building blocks, T_d of **pTPOTZ** is about 70 and 30 °C higher than those of **oTPOTZ** and **mTPOTZ**, respectively, which is consistent with intramolecular tensions in these molecules. Consequently, device fabrication of **xTPOTZ** is feasible through *vacuum* evaporation.



3.3 Optical Performance

Electronic absorption spectra of *xTPOTZ* in dilute solutions (10⁻⁶ ⁴⁰ mol L⁻¹ in CH₂Cl₂) comprise two bands around 270 and 230 nm, ascribed to combined $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions between

triazole and phenyls of **TPTZ** cores and $\pi \rightarrow \pi^*$ transition of phenyls in DPPO groups (Fig. 4 and Table 1). Obviously, ε , corresponding to transition probabilities, and peak ways englise of a 45 TPTZ core-originated absorptions for xTPOTZ are determined by conjugation degrees of TPTZ cores. In this case, with absorption of TPTZ at 270 nm as reference, the weaker absorption of oTPOTZ at 264 nm is perfectly consistent with its twisted TPTZ core, while the absorption band of mTPOTZ at 50 272 nm has the comparable coefficient, revealing the unchanged configuration of its TPTZ core due to mesa-substitution of DPPO groups. For pTPOTZ, this band bathochromicly shifts to 280 nm with enhanced coefficient, which should be ascribed to slight conjugation extension by para-substituted P=O groups. 55 Simultaneously, since the strong electron-withdrawing inductive effect of triazole on para-DPPO groups, the DPPO-attributed absorption of pTPOTZ is distinctly weaker than those of oTPOTZ and mTPOTZ, which reflects the more effective intramolecular electronic communications in *p***TPOTZ**. 60 Nevertheless, the energy levels of the first singlet states (S_1) for *x***TPOTZ** are identical as ~ 4.0 eV, estimated by their absorption edges, which are 0.16 eV lower than that of TPTZ due to electron-withdrawing effect of DPPO groups. In spin-coated thin

films, the fine structures of absorption spectra for **xTPOTZ**⁶⁵ remain with slight bathochromic shifts due to the limited aggregation, validating their excited energy preservation in solid states (Fig. S1).



Fig. 4 UV/vis absorption, fluorescence (FL) and phosphorescence (PH, inset) spectra of **xTPOTZ** in CH₂Cl₂ (10⁻⁶ M). PH spectra were measured at 77 K after a delay of 300 μ s.

The fluorescence (FL) spectrum of **TPTZ** in dilute solution consists of two peaks at 366 and 475 nm, corresponding to ⁷⁵ monomer and excimer emissions⁵⁰⁻⁵¹, respectively (Fig. 4, S2 and **Table 1**). Contrarily, only single-molecule emissions from dilute solutions of *x***TPOTZ** are observed around 367 nm, owing to suppressed intermolecualr aggregation by steric hindrance of peripheral DPPO groups. The wavelengths and profiles of monomer emission of *x***TPOTZ** and **TPTZ** are identical, in accord with their similar electronic states. However, in films, FL spectra of *x***TPOTZ** and **TPTZ** are exactly the same in whole range, including a main peak at 379 nm and a broad excimer emission from 400 to 700 nm. Compared to spectra in solution, st he bathochromic shift of 20 nm and enhanced excimer emissions

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reflect the stronger intermolecular interactions of xTPOTZ in solid states, which is beneficial to charge transport in their thin films.

- Significantly, phosphorescence (PH) spectra of **xTPOTZ** were ⁵ recorded at 77 K with a time-resolved approach to evaluate their triplet-state characteristics (inset in Fig. 4). Compared to **TPTZ**, DPPO-substitution in **xTPOTZ** only slightly changes the profiles of their PH spectra, implying the similar locations of their triplet states. Estimated from the 0-0 transitions, T₁ value of **mTPOTZ** ¹⁰ is as high as 3.0 eV, identical to that of **TPTZ**; while, T₁ levels of
- oTPOTZ and pTPOTZ reach to 2.95 eV. The negligible triplet

reduction of 0.05 eV should be ascribed to either structural relaxation of triplet excited state for **oTPOTZ** or slight conjugation extension by *para*-substitution: of $15\frac{1}{30}$ effects only and **pTPOTZ**, which is in accord with the negligible influence of P=O substitution on triplet energy of other unipolar systems.⁵² Consequently, T₁ values of **xTPOTZ** are comparable with that of the conventional high-energy-gap host *m*CP (2.95 eV) and ~0.3 eV higher than that of sky blue phosphor FIrpic (2.65 eV), ²⁰ affording effective suppression of exciton diffusion from EML in PHOLEDs.



Fig. 5 Contours and energy levels of frontier molecular orbitals of **xTPOTZ** and spin density distributions of their triplet states according to DFT calculation.

- 25 Therefore, with the feature of insulating linkage, DPPO substitution successfully restrains conjugation-extension induced energy loss of excited states for *x*TPOTZ, rendering their similar optical properties, which sequentially makes their optical
- properties, especially T₁ energy, ignorable for their device-³⁰ performance discrepancy. Meanwhile, although not as dramatic, *p***TPOTZ** exhibits the enchanced intramolecualr electronic communication at the same time of excited energy preservation,

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which would improve its electron injecting/transporting ability.

3.4 DFT simulation

To understand the nature of substitution effect of DPPO groups on optoelectronic properties of *x***TPOTZ**, the characteristics of s their ground states and T₁ states were simulated with DFT method at the level of 6-31G(d) (Fig. 5 and Table 1).

For TPTZ, electron cloud densities of its occupied molecular orbitals (MOs) and LUMO+2 are uniformly dispersed in whole molecule, while its LUMO and LUMO+1 are contributed by ¹⁰ triazole and respective two phenyls. It is showed that energy difference between the LUMO and LUMO+1 is negligible as 0.001 eV, making whole TPTZ involved in electron injection. Furthermore, energy levels of its HOMO and LUMO are -6.648 and -1.802 eV, revealing the strong electron injecting and hole 15 blocking ability. Contrarily, the asymmetrically twisted TPTZ core of oTPOTZ induces the different distribution of its unoccupied MOs. The LUMO is localized on triazole and two phenyls with smaller dihedral angles, while the LUMO+1 is dispersed on whole TPTZ core. Accordingly, the energy gap 20 between the LUMO and LUMO+1 remarkably increases to 0.3 eV. With planar TPTZ cores, the situation for unoccupied MO distributions of *m*TPOTZ and *p*TPOTZ is similar to that for TPTZ. Differently, the contributions of phenyls in their TPTZ cores to these MOs are increased due to the electron-withdrawing 25 inductive effect of P=O, giving rise to their dramatically reduced LUMO and LUMO+1 energy levels of -2.203 and -2.196 eV for mTPOTZ and -2.227 and -2.226 eV for pTPOTZ, respectively. Their HOMO and HOMO-1 are simultaneously decreased for 0.25 eV in comparison to those of TPTZ. Therefore, the 30 employment of DPPO groups indeed enhances the electron Table 1 Physical properties of xTPOTZ and TPTZ

injecting and hole blocking ability of *m***TPOTZ** and *p***TPOTZ**. Among *x***TPOTZ**, the lowest energy of unoccupied MOs for *p***TPOTZ** further manifest its strongest intramolecual View Article Online communications between DPPO and **TPTZ** segments on the ³⁵ basis of *para*-linkage.

It is noteworthy that with the predominant contributions to the unoccupied MOs, **TPTZ** cores of *x***TPOTZ** establish the main electron transport channels. Therefore, the increased distributions of unoccupied MOs on outer phenyls of their **TPTZ** cores would ⁴⁰ benefit the intermolecular charge exchange. In this sense, *p***TPOTZ** should be superior in electron transportation with more exposed configuration and more uniform distributions of unoccupied MOs on its **TPTZ** core, owing to its *para*substitution DPPO groups.

 T_1 energy levels of *xTPOTZ* were estimated as the energy gaps between their ground states and T₁ excited states, which are 2.975, 3.093 and 3.031 eV for oTPOTZ, mTPOTZ and *p***TPOTZ**, respectively. These values are in accord with optical analysis results and high enough for suppressing triplet exciton 50 diffusion in blue PHOLEDs. According to spin density distribution (SDD), T₁ states of TPTZ and oTPOTZ are more extended with the locations on triazole and two phenyl groups, which are overlapped with their LUMOs. Contrarily, the stronger inductive effect of DPPO groups in mTPOTZ and pTPOTZ 55 makes their T₁ states concentrated to triazole and one phenyl moieties and thereby thoroughly embedded in molecular frameworks. Considering the charge-exchange Dexter mechanism of triplet energy transfer, the shielded triplet states of *m*TPOTZ and *p***TPOTZ** would be superior in blocking triplet exciton 60 diffusion from EMLs in their devices.

1 1								
Absorption (nm)	Emission (nm)	S_1 (eV)	T_1 (eV)	$T_{\rm g}/T_m/T_d$	HOMO (eV)	LUMO (eV)	$E_{\rm R}^{\rm f}$	μ_{e}^{g} (cm ² V ⁻¹ s ⁻¹)
228, 263 ^a 228, 270 ^b	367 ^a 295_379 ^b	4.01 ^c 4.54 ^d	2.95° 2.96 ^d	-/273/429	-6.40 ^g	-3.26 ^g	0.565	4.1×10 ⁻⁶
228, 272 ^a 229, 278 ^b	367 ^a 295, 379 ^b	4.01 ^c 4.68 ^d	$3.00^{\rm e}$ $3.09^{\rm d}$	-/284/466	-6.64 ^g	-3.34^{g} -2.20^{d}	0.373	1.1×10 ⁻⁴
227, 281 ^a 228, 289 ^b	367 ^a 295, 379 ^b	3.98 ^c 4.64 ^d	2.95 ^e 3.03 ^d	-/320/500	-6.64 ^g -6.87 ^d	-3.46 ^g -2.23 ^d	0.379	3.4×10 ⁻⁴
222, 270 ^a 224, 281 ^b	366, 482 ^a 295, 379 ^b	4.16 ^c 4.99 ^d	3.00 ^e 3.10 ^d	-/232/259	-6.24 ^g -6.26 ^d	-3.22 ^g -1.18 ^d	0.277	-
	Absorption (nm) 228, 263 ^a 228, 270 ^b 228, 272 ^a 229, 278 ^b 227, 281 ^a 228, 289 ^b 222, 270 ^a 224, 281 ^b	Absorption (nm) Emission (nm) 228, 263 ^a 367 ^a 228, 270 ^b 295, 379 ^b 228, 272 ^a 367 ^a 229, 278 ^b 295, 379 ^b 227, 281 ^a 367 ^a 228, 289 ^b 295, 379 ^b 222, 270 ^a 366, 482 ^a 224, 281 ^b 295, 379 ^b	Absorption Emission S_1 (nm) (nm) (eV) 228, 263 ^a 367 ^a 4.01 ^c 228, 270 ^b 295, 379 ^b 4.54 ^d 228, 272 ^a 367 ^a 4.01 ^c 229, 278 ^b 295, 379 ^b 4.68 ^d 227, 281 ^a 367 ^a 3.98 ^c 228, 289 ^b 295, 379 ^b 4.64 ^d 222, 270 ^a 366, 482 ^a 4.16 ^c 224, 281 ^b 295, 379 ^b 4.99 ^d	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				

^{*a*} in CH₂Cl₂ (10⁻⁶ mol L⁻¹); ^{*b*} in film; ^{*c*} estimated according to the absorption edges; ^{*d*} DFT calculated results; ^{*e*} calculated according to the 0-0 transitions of the phosphorescence spectra; g calculated according to the equation HOMO/LUMO = 4.78 + onset voltage; ^{*f*} anion reorganization energy calculated by DFT method; ^{*g*} estimated according to field-dependent SCLC model on the basis of electron-transporting-only devices.

⁶⁵ Consequently, FMO and triplet-state locations of *x*TPOTZ are successfully adjusted in virtue of steric hindrance and inductive effects of DPPO groups and substitution position variation, which rationally corresponds to the improved electron affinity and exciton blocking ability of *m*TPOTZ and *p*TPOTZ.

70 3.5 Electrical Performance

Electrochemical analysis of **xTPOTZ** was performed to experimentally validate improved carrier injecting ability of these materials (Fig. 6 and Table 1). Reduction voltammograms of **TPTZ** consisted of one reversible peak at -2.00 V with an onset 75 voltage of -1.56 V, corresponding to the LUMO energy of -3.22

eV. The reduction behaviours of **oTPOTZ** and **mTPOTZ** are ascribed to their **TPTZ** cores, verified by their voltammograms similar to that of **TPTZ**. The onset voltages of -1.52 and -1.44 V

for the single reversible peaks of **oTPOTZ** and **mTPOTZ** at -⁸⁰ 1.67 and -1.60 V correspond to the LUMO energy levels of -3.26 and -3.34 eV, respectively. Compared to **TPTZ**, the 0.12 eV reduced LUMO of **mTPOTZ** can be rationally attributed to enhanced electron affinity of its **TPTZ** core by the electronwithdrawing inductive effect of P=O groups, which also

⁸⁵ neutralizes remedy the defect of *o*TPOTZ with twisted TPTZ core. As expected, the first reversible reduction peak of *p*TPOTZ dramatically shifts to -1.49 V with an onset voltage of -1.32 V, corresponding to the LUMO of -3.46 eV. Therefore, in comparison with *mesa*-substituted *m*TPOTZ, a further LUMO
⁹⁰ reduction of 0.12 eV for *p*TPOTZ is achieve by enhanced inductive effect of P=O groups at *para* positions of TPTZ, which is in accord with DFT simulated results. The amplified intramolecular interactions between TPTZ core and DPPO

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groups of *p***TPOTZ** sequentially result in its unique second reversible DPPO-attributed reduction peak at -2.06 V, revealing the auxiliary function of peripheral DPPO groups for electron injection and transportation in *p***TPOTZ**.

As ETMs, the cycle-to-cycle stability under reduction processes is one of the key indicators. The reduction voltammograms of *x*TPOTZ was measured in a range of -2.5-0 V with 10 times of repetition (Fig. S3). The peak position and profile of the curves are unchanged during whole cyclic processes, in indicating the excellent charge-discharge reversibility of *x*TPOTZ, which benefits to not only electron injection but also intermolecular electron transfer.



Fig. 6 Cyclic voltammograms of xTPOTZ and TPTZ measured in THF with tetra-n-butylammonium hexafluorophosphate as supporting electrolyte (0.1 mol L⁻¹) at the scanning rate of 100 mV S⁻¹.

On the other hand, according onset voltages of their irreversible oxidation peaks, the HOMO energy levels of **TPTZ** and **20 xTPOTZ** are estimated as -6.24, -6.40, -6.64 and -6.64 eV (**Table 1**), respectively, exhibiting the effect of DPPO substitution on hole blocking enhancement. Especially for **mTPOTZ** and **pTPOTZ**, their remarkably low-lying HOMOs make them favourable among the most efficient hole blocking ²⁵ materials, such as 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP, -6.50 eV) and TmPyPB (-6.68 eV).

The single-layer electron-only transporting devices of x**TPOTZ** were fabricated to estimate their intrinsic electron transporting characteristics with a configuration of ITO|LiF (1

- ³⁰ nm)|**xTPOTZ** (100 nm)|LiF (1 nm)|Al, in which LiF served as electron-injecting layer. Ampere-volt (*I-V*) characteristics of these electron-only transporting devices reveal the same dependence on molecular structures of **xTPOTZ**, as deduced from single crystal data and DFT simulation results (Fig. 7). Current density (*J*) of
- ³⁵ pTPOTZ-based devices was about one and two orders of magnitude larger than those of mTPOTZ and oTPOTZ-based devices, respectively. The current density in these devices follows the field-dependent space charge limited current (SCLC) model of Mott-Gurney law, which is given as⁵³:

⁴⁰
$$J_{SCLC} = \frac{9}{8} \varepsilon \varepsilon_0 \mu_0 \exp\left(0.89\beta \sqrt{\frac{V}{d}}\right) \frac{V^2}{d^3} \qquad \text{eq.1}$$

where V is electrical voltage, d is film thickness, μ_0 is the average mobility, ε_0 is the permittivity of free space (8.854×10⁻¹² F m⁻¹), and ε is dielectric constant of the film The state of the other of the film The state of the other of the film The state of the other of the other of the film of the film of the film of the other of the other of the film of the film of the film of the other other other of the film of th

It is showed that APO groups as insulating linkage with strong polarizability can be promising building blocks for high-energygap ETMs. Although their steric configurations would impede ⁵⁵ intermolecular interactions, at appropriate substitution position, APO groups can increase molecular electron affinity and assist electron transport on the basis of enhanced intramolecualr electronic coupling. Therefore, PO modification can indeed effectively integrate and harmonize high excited-state energy and ⁶⁰ electron transporting ability for high-energy-gap ETMs, as evidenced by **mTPOTZ** and **pTPOTZ** with the T₁ value of ~3.0 eV and μ_e on the order of 10^{-4} cm² V⁻¹ s⁻¹.



Fig. 7 *I-V* characteristics of **xTPOTZ**-based electron-only devices in the range of operating voltages for their PHOLEDs. Symbols show the experimental data, while lines are the fitting curves according to field-dependent SCLC model.

3.6 Device Performance

Encouraged by the excellent optoelectronic properties of **xTPOTZ**, especially their high T₁ value of ~3.0 eV, **xTPOTZ** are competent as ETMs in sky blue PHOLEDs. Therefore, PHOLEDs **A**, **B** and **C** by employing *m*CP as host and FIrpic as sky blue phosphor were fabricated with the most conventional trilayer configuration of ITO|MoO₃ (10 nm)|TAPC (70 nm)|*m*CP:FIrpic (10%, 20 nm)|*x***TPOTZ** (35 nm)|LiF (1 nm)|Al, where TAPC served as hole transporting/exciton blocking layer and *x***TPOTZ** was utilized as electron transporting/exciton blocking material (Scheme 2). The control device **D** with TmPyPB as ETL was also fabricated for comparation. ⁸⁰ Electroluminescence (EL) spectra were ascribed to the pure skyblue emissions from FIrpic with the main peak at 475 nm and favorable Commission Internationale Ed I'eclairage (CIE) coordinates of (0.15, 0.30) (inset in **Fig. 8a**), reflecting the

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effective exciton confinement in EML.



Scheme 2 Configuration and energy level diagram of PHOLEDs and the chemical structures of employed materials.

- According to energy levels diagram of these sky blue PHOLEDs (Scheme 2), the electron-injecting barrier between FIrpic and cathode was 0.8 eV, which was 0.5 eV lower than that between *m*CP and cathode. In this case, the dominant electron ¹⁰ injection channel in EML would be direct charge capture by FIrpic. It is noteworthy that the LUMO energy levels of **xTPOTZ** are between the LUMO and Femi energy levels of FIrpic and cathode, dividing the energy gap into two parts of ~0.4 eV. In this case, **xTPOTZ** can facilitate the direct electron ¹⁵ capture on FIrpic as intermediates to provide two sequential electron-transfer steps with reduced injection barriers. As
- expected, **xTPOTZ** endowed their devices with the extremely low turn-on voltages of ~2.6 V, which were equivalent with the photon energy as 2.65 eV of FIrpic-originated emission according ²⁰ to its first emission peak at 475 nm (**Fig. 8a** and **Table 2**). Compared to **D**, the threshold voltages of **A**, **B** and **C** were
- dramatically reduced for 1.0 V, reflecting the barrier-free electron injection in these devices through *x***TPOTZ** with more low-lying LUMOs. Furthermore, at practical luminance of 100 and 1000 cd ²⁵ m⁻², operating voltages of C with *p***TPOTZ** as ETL were less
- than 3.8 and 5.2 V, respectively, which were 0.7 V lower than those of **B**. On account of the major carrier in these devices as hole, the highest μ_e of *p***TPOTZ** facilitated charge flux balance in its devices and enhance exciton recombination for high
- ³⁰ luminance under the same voltages. For the same reason, **oTPOTZ** with the lowest μ_e induced the smallest luminance of its devices. This correlation was further indicated by the proportionality between brightness of **A**, **B** and **C** and their *J*. The tendency of *J* for these devices was approximately consistent
- ³⁵ with that of *I-V* characteristics for **xTPOTZ**-based electron-only transporting devices, further verifying the effectiveness of **xTPOTZ** to electron transporting and hole blocking. It is notable





Fig. 8 a) J-Voltage-Luminance characteristics and EL spectra (inset) of mCP and FIrpic based devices A, B, C and D with xTPOTZ and TmPyPB as ETL; b) Efficiencies curves of A, B, C and D versus luminance.

The uniform triplet energy and triplet-state locations of *x***TPOTZ** exclude the correlation of triplet characteristics with their various device performance, establishing the direct correspondence between charge flux balance and EL efficiencies 50 and efficiency stability. Consequently, beneficial to the most balanced carrier flux by pTPOTZ with the strongest electron injecting and transporting ability, the efficiencies of C were the highest among these devices with maxima of 39.3 cd A⁻¹ for current efficiency (CE), 34.0 lm W⁻¹ for power efficiency (PE) 55 and 19.9% for EQE, which were improved for more than 50% compared to those of TmPyPB-based D (Fig. 8b and Table 2). The maximum CE and EQE of C were achieved at a practical luminance more than 100 cd m⁻², accompanied with alomost negligible roll-offs less than 4% at 1000 cd m^{-2} . Because of 3 60 times low μ_e for **mTPOTZ**, the maximum efficiencies of its device **B** were remarkably reduced to 23.8 cd A^{-1} , 20.1 lm W^{-1} and 11.8%, respectively, which were only about a half of those of C, but 1.6 folds of those of A. The worst EL performance of A among these devices should be ascribed to its most unbalanced 65 charge flux, due to the lowest μ_e of *o***TPOTZ** among *x***TPOTZ**. At high voltages, J of these devices followed SCLC model, in

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direct proportion to charge mobility of whole organic semiconductor layer (eq. 1). Considering μ_h of TAPC as hole transporting layer (HTL) on order of 10^{-3} cm² V⁻¹ s⁻¹, which is three orders of magnitude larger than μ_e of **oTPOTZ** as ETL, s hole would be extremely excessive in **A** at high voltages, worsening charge unbalance and triplet exciton-polaron quenching (TPQ) in its emissive layer. Therefore, serious rolloffs of **A** at 1000 cd m⁻² were 5 and 20 folds of those of **B** and **C**, respectively. The worse efficiency stability of **B** than that of **C** ¹⁰ further verified this correlation between charge flux balance and efficiency roll-offs.

Consequently, compared to the classical high-energy-gap ETM **TmPyPB**, *p***TPOTZ** endowed its conventional *m*CP and FIrpic based sky blue PHOLEDs with the much reduced driving ¹⁵ voltages and the 1.5-fold larger efficiencies, which should be the cumulative result of its triplet energy of ~3.0 eV, the low-lying LUMO at -3.5 eV and high μ_e on order of 10⁻⁴ cm² V⁻¹ s⁻¹.

Table 2 EL performance of mCP and FIrpic-based devices A-D.

ETM	Operating	Maximum	Efficiency Roll-Offs (%) ^c			
	Voltage $(V)^{a}$	Efficiencies ^b	CE	PE	EQE	
o TPOT	<2.6, <4.9,	16.9,14.3,8.3	<9, <75	<31, <90	<10, <75	
Z	<9.3					
mTPOT	<2.7, <4.5,	23.8, 20.1,	-, <15	<17, <50	-, <15	
Z	<6.3	11.8				
<i>p</i> TPOT	<2.5, <3.8,	39.3, 34.0,	-, <4	<9, <40	-, <4	
Ż	<5.6	19.9				
TmPyP	<3.4, <4.9,	24.7, 12.4,	-, <0.5	-, <4	-, <0.5	
B	<6.8	13.1				

^{*a*} in the order of onset, 100 and 1000 cd m⁻²; ^{*b*} in the order of CE (cd A⁻¹), ²⁰ PE (lm W⁻¹) and EQE (%); ^{*c*} in the order of 100 and 1000 cd m⁻².

4. Conclusions

In summary, a series of TPPO substituted 1,3,5-triazole derivatives **xTPOTZ** were designed and prepared as n-type semiconductors. APO modification remarkably enhances the ²⁵ morphological and thermal stability of **xTPOTZ** with T_m beyond 250 °C and T_d more than 400 °C. As an insulating polar group, DPPO substituents endow **xTPOTZ** with the preserved optical properties of their **TPTZ** cores, such as T₁ of ~2.95 eV for effective exciton blocking, and improved electrical performance, ³⁰ including higher electron affinity and mobility. Both DFT simulation and CV analysis showed the low-lying LUMO and

- HOMO energy levels of *x***TPOTZ**, compared to those of **TPTZ**, revealing the enhanced electron injecting and hole blocking ability after APO modification. It is verified that the substitution
- ³⁵ position of DPPO groups in *x*TPOTZ correlates to their electrical performance. The twisted configuration of *o*TPOTZ by steric hindrance of *ortho*-substituted DPPO groups rendered its weakest electron affinity and smallest electron mobility, while planar *m*TPOTZ and *p*TPOTZ achieve the LUMO and HOMO energy
- ⁴⁰ levels of about -3.4 and -6.6 eV, respectively, accompanied with the extremely high μ_e on the order of 10^{-4} cm² V⁻¹ s⁻¹. Among **xTPOTZ**, **pTPOTZ** shows the strongest electroactivity, owing to its exposed TPTZ core and enhanced intramolecular electronic communication through its *para*-substitution configuration. On
- ⁴⁵ the basis of trilayer conventional *m*CP and FIrpic-based sky blue PHOLEDs, *p***TPOTZ** revealed its superiority as ETL with the extremely low driving voltages of 2.5 V for onset and 3.8 V at 100 cd m⁻² and the favorable EQE up to 19.9%, as well as

reduced roll-offs. This work demonstrated an effective strategy of 50 APO modification for enhancing electrical performance of n-type semiconductors without influencing their optical property of 202993C

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Notes and references

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Triazole and triphenylphosphine oxide (TPPO) hybrids **xTPOTZ** were constructed as electron-transporting materials in blue phosphorescent light-emitting diodes to achieve high triplet energy beyond 2.95 eV, low-lying lowest unoccupied molecular orbitals at ~-3.4 eV and high electron mobility up to 3.4×10^{-4} cm² V⁻¹ s⁻¹, which are impressive among high-energy-gap electron-transporting materials reported so far. As the result, *p***TPOTZ** endowed its typical *m*CP and FIrpic-based blue PHOLEDs with the ultralow onset voltage of 2.6 V and favourable external quantum efficiency up to ~13%, revealing the effectiveness of APO modification for high-performance ETM development.

