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Spirobifluorene-based oligopyridine derivatives as

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light-emitting diodes

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Abstract:

The electron-transporting materials (ETMs), 2,7-bis(3,5-di(pyridin-3-yl)phenyl)-9,9'-spirobi[fluorene] (3-4PySF) and 2,7-bis(3,5-di(pyridin-4-yl)phenyl)-9,9'-spirobi[fluorene] (4-4PySF) were designed and synthesized by combining spirobifluorene moiety with di(pyridine-3-yl)phenyl and di(pyridine-4-yl)phenyl, respectively. The spirobifluorene moiety improves materials' rigid twisted structure to ensure the morphological stability of amorphous film, and pyridine acts as electron acceptor to enhance electron-transporting ability of materials. The dependence of electron-transporting property on the position of substituted pyridine rings was studied. The melting point (T_m) of 4-4PySF is estimated to be 41 °C higher than that of 3-4PySF. And the higher current density in the

electron only devices exhibited by 4-4PySF revealed the effect of nitrogen atom position on the charge-transporting properties. Green PhOLEDs based on bis(2-phenylpyridine)iridium(III)(2,2,6,6-tetramethylheptane-3,5-diketonate)

(Ir(ppy)₂tmd) as the emitter and 3-4PySF, 4-4PySF and 1,3,5-tris(N-phenylbenzimid azol-2-yl-benzene (TPBi) as ETMs were fabricated. Compared to the device based on the conventional ETM TPBi, the devices based on new ETMs exhibited a higher maximum external quantum efficiency (EQE) of 20.5% and a lower turn-on voltage (V_{on}) of 2.6 V.

Keywords:

electron-transporting material; organic light-emitting diode; oligopyridine; spirobifluorene; intermolecular interaction.

1. Introduction

Since the milestone work of OLEDs in 1987 by Tang and VanSlyke, organic light-emitting diodes (OLEDs) have experienced rapid development due to its merits in large-area and flexible devices.[1-4] Efficiency of OLEDs depends on the transporting and recombination effectively of electron and hole. By reason that electron mobility in organic materials are usually several orders of magnitude lower than hole mobility,[5] many researchers are devoted to developing electron-transporting materials with high electron mobility.[6, 7] Pyridine-based compounds have been synthesized because of strong electron-accepting character of pyridine, and the ability to change the electrical properties of the molecule by changing the substitution sites.[8, 9] Kido et al. reported that changing the position of

nitrogen atoms on oligopyridine derivatives can change the intermolecular weak hydrogen bonds, thereby adjusting the horizontal orientation in amorphous organic semiconductor films and significantly modulating electron mobility.[10, 11] However, these materials often own a planar structure, and excessive π - π stacking between the molecules during deposition leads to a rough surface.[12] On the other hand, the spirobifluorene has rigid twisted structure that provides a high triplet energy (T_1) and a high glass transition temperature (T_g), which is beneficial to maintaining the morphological stability.[13, 14] It is promising to synthesize electorn-transporting materials by combining oligopyridine and spirobifluorene.

In this study, we synthesized 3-4PySF and 4-4PySF by combining di(pyridine-3-yl)phenyl and di(pyridine-4-yl)phenyl with spirobifluorene, respectively. The only difference between 3-4PySF and 4-4PySF is the substitution of the nitrogen atoms on the pyridine. The effect of nitrogen position of the pyridine on photophysical properties, thermal properties and the carrier transport were studied. Compared to 3-4PySF, 4-4PySF possesses a higher melting point, indicating stronger intermolecular forces between molecules. By electron only devices, it was found that the electron mobility of 4-4PySF is higher than that of 3-4PySF. Green PhOLEDs based on 3-4PySF and 4-4PySF were fabricated, and a maximum EQE of 20.5%, a lowest turn-on voltage of 2.6 V were achieved, which were superior to TPBi-based comparison device.

2. Experimental

2.1. General

Electrospray ionization mass spectroscopy in positive ion mode was performed on a Bruker Solarix XR Fourier Transform Ion Cyclotron Resonance Mass Spectrometer. The ¹H NMR and ¹³C NMR spectra were recorded on Bruker 500 MHz NMR spectrometer. Elemental analysis was measured on a VARIO elemental analyzer from Elementar Analysensysteme GmbH. DSC was performed on a PerkinElmer Diamond DSC Pyris instrument while TGA was recorded on a SEIKO EXSTAR 6000 TG/DTA 6200 unit under nitrogen atmosphere at a heating rate of 10° C/min. UV-vis absorption spectra were measured by using a Perkin-Elmer Lambda 35 spectrometer. Emission spectra were recorded by using Hitachi F7000 fluorescence spectrophotometer. The surface roughness of the film was performed on a conductive atomic force microscope (CAFM, SEIKO SPA300HV). Cyclic voltammetry was measured by using a CHI600C voltammetric analyzer with tetrabutylammonium hexafluorophosphate (TBAPF₆, 0.1 M) as the supporting electrolyte and ferrocene as an internal standard, in a nitrogen-purged dichloromethane (CH₂Cl₂) or DMSO solution at room temperature. The conventional three electrodes were a platinum working electrode, a platinum wire auxiliary electrode, and a Ag/AgCl wire pseudo reference electrode. HOMO level in film state was estimated by using ultraviolet photoelectron spectroscopy (AXIS Supra) from Kratos Analytical Ltd. The current density and voltage characteristics of OLEDs were obtained by using a computer controlled Keithley 2611 Sourcemeter. The luminance characteristics of OLEDs were recorded on a SRC-600 spectroradiometer (EVERFINE Corporation).

2.2. Materials

dipyrazino[2,3-f:2',3'-h]quinoxaline-2,3,6,7,10,11-hexacarbonitrile	(HAT-CN),
1,1-bis[4-[N,N-di(p-tolyl)-amino]phenyl]-cyclohexane	(TAPC),
tris(4-(9H-carbazol-9-yl)phenyl)-amine	(TCTA),

2,4-diphenyl-6-bis(12-phenylindolo)[2,3-a]carbazole-11-yl)-1,3,5-triazine (DIC-TRZ),

bis (2-phenyl pyridine) iridium (III) (2,2,6,6-tetramethyl heptane-3,5-diketonate)

(Ir(ppy)₂tmd), and 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBi) were commercially available and used without further purification.

2.3. Synthesis and characterization

Synthesis of 3,3'-(5-chloro-1,3-phenylene)dipyridine (1):A mixture of3,5-dibromochlorobenzene(18.5mmol),

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (39 mmol) and K_2CO_3 (93 mmol) were mixed in a flask containing nitrogen-saturated 1,4-dioxane (350 mL) before 1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (PdCl₂(dppf)) (0.38 g) was added. The resulting mixture reacted for 8.0 h and then purified by silica-gel column chromatography.

3,3'-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3-phenylene)dipyridine (2): Compound (1) (48.7 mmol), bis(pinacolato)diboron (54 mmol) and KOAc (122 mmol) were mixed in a flask containing nitrogen-saturated 1,4-dioxane (130 mL) before phenylallylchloro[1,3-bis(diisopropylphenyl)imidazole-2-ylidene]palladium(II) (Pd(IPr)(cin)Cl) (0.35 g) was added. The resulting mixture reacted for 3.0 h and then purified by silica-gel column chromatography. Synthesis of 3-4PySF: Compound (2) (34.1 mmol), 2,7-dibromo-9,9 ' -spirobifluorene (15.8 mmol) and K₂CO₃ (79 mmol) were mixed in a flask containing nitrogen-saturated 1,4-dioxane (120 mL) before PdCl₂(dppf) (0.3 g) was added. The resulting mixture reacted for 2.0 h and then purified by silica-gel column chromatography. ¹H NMR (500 MHz, CDCl₃): δ 8.86 (d, *J* = 2.0 Hz, 4H), 8.62 (dd, *J* = 4.8, 1.5 Hz, 4H), 8.02 (d, *J* = 7.9 Hz, 2H), 7.89 (ddd, *J* = 8.7, 5.5, 3.4 Hz, 6H), 7.75 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.63 (dd, *J* = 3.9, 1.4 Hz, 6H), 7.39 (ddd, *J* = 12.7, 7.7, 2.8 Hz, 6H), 7.15 (td, *J* = 7.5, 0.8 Hz, 2H), 7.01 (d, *J* = 1.4 Hz, 2H), 6.86 (d, *J* = 7.6 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 150.29, 148.87, 148.39, 148.25, 142.91, 141.90, 141.14, 140.37, 139.32, 136.26, 134.64, 128.08, 128.03, 127.36, 125.84, 125.03, 124.18, 123.61, 122.84, 120.72, 120.34, 66.24. HRMS (ESI, m/z): [M + H]+, calcd for C₅₇H₃₆N₄, m/z = 777.301274, found m/z = 777.298694; Anal. Calc. for C₅₇H₃₆N₄: C, 88.12; H, 4.67; N, 7.21. Found: C, 88.09; H, 4.66; N, 7.16.

Synthesis of 4-4PySF: Compound 4-4PySF was synthesized by the same procedure as described above for 3-4PySF using pyridin-4-ylboronic acid. ¹H NMR (500 MHz, CDCl₃): δ 8.68 (d, *J* = 5.3 Hz, 12H), 8.03 (d, *J* = 7.9 Hz, 3H), 7.89 (d, *J* = 7.6 Hz, 3H), 7.72 (ddd, *J* = 10.6, 8.6, 1.4 Hz, 12H), 7.51 (d, *J* = 5.5 Hz, 12H), 7.41 (t, *J* = 7.5 Hz, 3H), 7.16 (t, *J* = 7.5 Hz, 3H), 7.00 (d, *J* = 1.2 Hz, 3H), 6.87 (d, *J* = 7.6 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 150.33, 150.30, 148.23, 147.83, 143.07, 141.93, 141.19, 140.26, 139.82, 128.08, 128.06, 127.46, 126.55, 124.72, 124.22, 122.84, 121.87, 120.79, 120.34, 66.28. HRMS (ESI, m/z): [M + H]+, calcd for C₅₇H₃₆N₄, m/z = 777.301274, found m/z = 777.301608; Anal. Calc. for C₅₇H₃₆N₄: C, 88.12; H, 4.67; N, 7.21. Found: C, 87.81; H, 4.66; N, 7.17.

2.4. Device fabrication

The indium-tin-oxide (ITO) anode with a sheet resistance of $14 \ \Omega^{-1}$ was commercially available. Before the deposition of organic layers, the ITO substrate was cleaned successively with deionized water, acetone and ethanol. The organic and cathode layers were evaporated in same chambers, the base pressure of which is lower than 8 × 10⁻⁴ Pa. The active area for all devices was 3.14 mm². The organic and Al layers were thermally evaporated at a rate of 0.1–0.2 nm/s, while that of LiF layer was 0.01 nm/s.

3. Results and discussion

3.1. Synthesis and characterization

Two different types of electron-transporting materials were synthesized as shown in **Scheme 1**. The difference between 3-4PySF and 4-4PySF is the positions of the nitrogen atom on the pyridine rings, 3-4PySF is a meta-substituted nitrogen atom, and 4-4PySF is a para-substituted nitrogen atom. Two materials were characterized by electrospray ionization mass spectroscopy (ESI-MS), ¹H NMR, ¹³C NMR, elemental analysis and single-crystal analysis (as shown in supporting information).



Scheme 1. The synthesis process of the 3-4PySF and 4-4PySF.

3.2. Theoretical calculations

As shown in **Figure 1**, the highest occupied molecular orbital (HOMO) distribution and the lowest unoccupied molecular orbital (LUMO) distributions of 3-4PySF and 4-4PySF were carried out by Gaussian 09 software with the 6-31G(d, p) basis set. The electronic calculation results of 3-4PySF and 4-4PySF showed few differences. The HOMO was dispersed over the electron-rich spirofluorene moiety, while the LUMO was more distributed on the phenyl moiety, suggesting high electron mobility. After structural optimization, the corresponding energy levels were calculated by using the same theory. As a result, the HOMO energy levels of the 3-4PySF and 4-4PySF were calculated at -5.7 and -5.8 eV, respectively. The LUMO energy levels were calculated to -1.6 eV for 3-4PySF and -1.7 eV for 4-4PySF. To further explore the electron

injection ability, the total self-consistent field density of 3-4PySF and 4-4PySF were performed by using the electrostatic potential (ESP) method by Singh and Kollman.[15, 16] As illustrated in Figure 1, the high electronegativity region was concentrated on the nitrogen atom of pyridine, which was conducive to forming the coordination effect with metals, thereby efficiently enhancing the electron injection from the cathode.[17]



Figure 1. The HOMO, LUMO distributions of 3-4PySF and 4-4PySF. The isosurface of 3-4PySF ESP and 4-4PySF ESP.

3.3. Photophysical properties and electrochemical properties

The room-temperature ultraviolet-visible (UV-Vis) absorption spectra and photoluminescence (PL) spectra of 3-4PySF and 4-4PySF in chloroform (CHCl₃) (10^{-5} M) and film state were measured to investigate their photophysical properties, as shown in **Figure 2a** and **Table 1**. In solution, 3-4PySF exhibited two absorption peaks at 310 nm and 334 nm, respectively, corresponding to the π - π * transition of the fluorene units in spirobifluorene[18] and indicating the presence of electronic coupling between the spiobifluorene and the phenyl group.[19, 20] Compared with

the absorption spectrum in solution, the absorption spectrum in neat film showed a small red shift. The two absorption peaks moved to 312 nm and 336 nm, respectively, indicating the twisted structure of spirobifluorene inhibited the formation of π - π stacking of 3-4PySF. The absorption peaks of 4-4PySF in solution and film state were located at 309 nm, 333 nm, 313 nm and 339 nm, respectively, which were close to the absorption peaks of 3-4PySF. But 4-4PySF exhibited a bigger red shift in absorption from solution to thin film compared to 3-4PySF. The band gap E_g determined from the band edge of the UV-vis spectra were 3.34 eV for 3-4PySF and 3.29 eV for 4-4PySF.

As for the PL spectra, the fluorescence peaks of 3-4PySF in CHCl₃ and the film state were 369 nm and 401 nm, respectively. The fluorescence peaks of 4-4PySF were identical to that of 3-4PySF, which were also located at 369 nm and 401 nm, respectively. Compared to their similar absorptions in solution and film state, the thin film fluorescence emission showed significant red-shift comparing those in solution, indicating the existence of the interaction between the molecules in the solid state. [21, 22] For the purpose of studying the interaction between molecules, single crystal structural analysis of the 3-4PySF was performed using single crystal X-ray diffractometer. As shown in **Figure S1** (Supplementary Information), the intermolecular weak H-bonding interactions with a distance of 0.260 nm were confirmed. The interaction between molecules made the molecules pile up tightly.

In order to confirm the triplet energy (T_1) of 3-4PySF and 4-4PySF, the phosphorescence spectra of compounds in a frozen 2-methyl-tetrahydrofuran (10^{-5} M) at 77 K were measured with a 1 ms delay. From those low-temperature emission

spectra, we obtained T_1 of 2.44 eV for both materials (e.g. 3-4PySF and 4-4PySF). This result suggested that both materials have potential as electron-transporting materials in green phosphorescent devices.

For obtaining the relative energy levels of 3-4PySF and 4-4PySF, the oxidation/reduction potentials dichloromethane/ were measured in the dimethylsulfoxide (DMSO) solution using cyclic voltammetry (CV), as depicted in Figure 2b. The HOMO and LUMO energy levels of the compounds could be estimated by comparing the difference between the onset potentials for oxidation and reduction of the materials and the ferrocene (4.8 eV below vacuum).[23] Using an empirical formula $(E_{HOMO} = -(E_{ox} - E_{Fc/Fc^+}) eV + (-4.8) eV)$, the HOMO of 3-4PySF and 4-4PySF could be calculated to be -5.9 eV and -6.0 eV, respectively. And the LUMO levels of 3-4PySF and 4-4PySF were figured to be -2.3 eV and -2.4 eV, respectively, by using $(E_{LUMO} = -(E_{re} - E_{Fc/Fc^+}) eV + (-4.8) eV)$. Meanwhile, the HOMO energy levels of two materials in film were estimated by ultraviolet photoelectron spectroscopic (UPS) measurements (Figure S2 and S3, Supplementary Information), both at -5.9 eV. The LUMO energy levels determined via the subtraction of the $E_{\rm g}$ from the HOMO energy levels were -2.6 eV for both compounds. The difference between the energy level in the solution state and the film state could be due to the interaction between molecules in the film state.



Figure 2. (a) Absorption, fluorescence, and phosphorescence spectra of 3-4PySF and 4-4PySF. (b) The CV curves of 3-4PySF and 4-4PySF at a scan rate of 100 mV s^{-1} .

Table 1. Physical	properties of	3-4PySF and	4-4PySF

Material	$\lambda_{abs}^{a)}$ [nm]	$\lambda_{abs}^{b)}$ [nm]	$\lambda_{PL}^{a)}$ [nm]	$\lambda_{PL}^{b)}$ [nm]	$T_{\rm m}$ [°C]	HOMO ^{c)} / HOMO ^{d)}	LUMO ^{c)} / LUMO ^{d)}	$E_{\rm T}$ [eV]
						[eV]	[eV]	
3-4PySF	310, 334	312, 336	369	401	383	-5.9/-5.9	-2.6/-2.3	2.44
4-4PySF	309, 333	313, 339	369	401	424	-5.9/-6.0	-2.6/-2.4	2.44

^{a)}Measured in CHCl₃; ^{b)}Measured in neat film; ^{c)}Measured using ultraviolet photoelectron spectroscopic, LUMO^{c)} = HOMO^{c)} + E_g ; ^{d)}Measured using CV.

3.4. Thermal properties and film morphology

The thermal properties of 3-4PySF and 4-4PySF were estimated by thermogravimetric

analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen atmosphere (**Figure S4-S7**, Supplementary Information). The decomposition temperature (T_d) were observed to be 462 °C and 472 °C for 3-4PySF and 4-4PySF, respectively, indicating a high thermal stability. The melting (T_m) of 4-4PySF was measured to be 424 °C, which was 41 °C higher than that of 3-4PySF (**Figure 3**). The apparent difference in T_m between two materials may be mainly due to the difference in H-bonding interactions between two materials in the solid state,[11] suggesting that 4-4PySF possessed stronger intermolecular H-bonding with respect to 3-4PySF. The glass transition temperature (T_g) of 3-4PySF was 176 °C, which was higher than those commonly used electron-transporting materials such as TPBi ($T_g =$ 124 °C). The high T_g is derived from the rigid and twisted molecular structure, which helps to maintain the morphological stability of amorphous film during thermal evaporation and contribute to enhancing the device lifetime.



Figure 3. DSC plots of 3-4PySF and 4-4PySF.

As shown in **Figure 4**, the morphology of films of 3-4PySF and 4-4PySF were measured by atomic force microscopy (AFM) in tapping mode. The 50 nm thick films

of 3-4PySF and 4-4PySF deposited on silica glass exhibited root-mean-square roughness ($R_{\rm rms}$) of only 0.337 nm and 0.307 nm, respectively. Amorphous smooth stable films, which were resulted from the rigid twisted spirobifluorene moiety hindering the π - π stacking between the molecules, helped to the preparation of stable OLEDs.[24]



Figure 4. 3D topography images and $R_{\rm rms}$ values of 50 nm thick films of (a) 3-4PySF ($R_{\rm rms}$ 0.337 nm), and (b) 4-4PySF ($R_{\rm rms}$ 0.307 nm).

3.5. Device characteristics

To further study the compound's electron-transporting properties, three single-carrier devices were fabricated. They had the device structure of indium tin oxide (ITO)/BCP (10 nm)/3-4PySF or 4-4PySF or TPBi (30 nm)/LiF/Al, respectively. Here, the purpose of BCP in electron only devices was to block the injection of hole carriers from the ITO electrode. **Figure 5** shows the current density-voltage curves of three single charge device. Current density of the 4-4PySF based device was higher than that of 3-4PySF and TPBi based devices at the same voltage. Since 3-4PySF and 4-4PySF were extremely similar in terms of optical properties and energy levels, the difference

in electron-transporting ability was likely to be caused by different molecular packings during deposition. It's worth noting that the only difference between derivatives is the position of the nitrogen atom on peripheral pyridine rings. Compared with the nitrogen atom in the meta-position, the nitrogen atom in the para-positon could provide stronger intermolecular H-bonding in the film state, hence increasing the horizontal molecular orientation in the film state, and finally leading to an enhancement in electron-transporting ability, as suggested by Kido et al.[10, 12] Therefore, 4-4PySF possessing the para-position nitrogen atom exhibited strongest electron-transporting capability in three single-carrier devices.



Figure 5. Current density-voltage characteristics of electron-dominant device: ITO/BCP (10 nm)/3-4PySF or 4-4PySF or TPBi (30 nm)/LiF/Al.

To verify the performance of 3-4PySF and 4-4PySF as ETMs, Ir(ppy)₂tmd-based green phosphorescent OLEDs were fabricated. The device based on the conventional electron-transporting material TPBi was also prepared for reference. **Figure 6** shows the chemical structures and energy diagram of materials used in devices. The device structures are listed as follows:

Device A: ITO/HAT-CN (2 nm)/TAPC (60 nm)/TCTA (5 nm)/DIC-TRZ:Ir(ppy)₂tmd (7 wt%, 20 nm)/3-4PySF (40 nm)/LiF/Al

Device B: ITO/HAT-CN (2 nm)/TAPC (60 nm)/TCTA (5 nm)/DIC-TRZ:Ir(ppy)₂tmd (7 wt%, 20 nm)/4-4PySF (40 nm)/LiF/Al

Device C: ITO/HAT-CN (2 nm)/TAPC (60 nm)/TCTA (5 nm)/DIC-TRZ:Ir(ppy)₂tmd (7 wt%, 20 nm)/TPBi (40 nm)/LiF/A1

where HAT-CN was used to modify ITO to enhance hole injection from ITO to TAPC, TAPC and TCTA were used as hole-transporting materials. The green phosphorescent emitter Ir(ppy)₂tmd co-deposited with the TADP hose material DIC-TRZ was chosen to be emitting materials.

As shown in **Figure 7** and **Table 2**, the turn-on voltages (V_{on}) of 2.6 V, 2.8 V obtained from the devices based on 3-4PySF and 4-4PySF, respectively, were lower than those of the device based on TPBi (2.9 V), indicating superior electron injection abilities of both materials. Among the three devices, device **A** possessed the best performance. The maximum current efficiency ($\eta_{CE, max}$) was 76.6 cd/A for device **A**, this efficiency data corresponded to 20.5% of EQE. Since the superior electron injection injection capability, the maximum power efficiency ($\eta_{PE, max}$) of device **A** was 83.6 lm/W. However, it may be due to the high electron-transporting property of 4-4PySF that caused carrier imbalance in the device, the device **B** did not perform as well as device **A**. But, the parameters of device **B** were comparable to those of TPBi-based comparison device. The $\eta_{CE, max}$ and $\eta_{PE, max}$ were 68.8 cd/A and 62.7 lm/W for device

B, 69.8 cd/A and 59.5 lm/W for device **C**, respectively, and correspond to 18.3% and 18.5% of EQEs for device **B** and **C**, respectively. Based on these results, we believe that both 3-4PySF and 4-4PySF could provide fairly good device performances because of their superior electron injection and electron-transporting properties.



Figure 6. Chemical structures, and energy diagram of materials.



Figure 7. (a) Current density-voltage and luminance-voltage, (b) power efficiency-luminance, (c) current efficiency-luminance, (d) external quantum efficiency- luminance curves and (e) electroluminescence (EL) spectra obtained from Device A, Device B and Device C.

	$V_{\mathrm{on}}^{\mathrm{a})}$	$\eta_{ ext{CE, max}/1000/10\ 000}^{ ext{b})}$	$\eta_{ ext{PE, max}/1000/10000}^{ ext{ b)}}$	EQE, max/1000/10 000 ^{b)}	CIE ^{c)}
	[V]	$[cd A^{-1}]$	$[\operatorname{lm} W^{-1}]$	[%]	(x,y)
Α	2.6	76.6/75.1/68.2	83.6/47.9/26.2	20.5/20.1/18.2	(0.35, 0.62)
B	2.8	68.8/67.5/55.7	62.7/31.1/18.0	18.3/17.9/14.8	(0.35, 0.62)
С	2.9	69.8/68.1/56.4	59.5/29.1/17.1	18.5/18.0/15.0	(0.34, 0.62)

Table 2. List of device performances

^{a)}At 1 cd m⁻²; ^{b)}Maximum, at 1000 cd m⁻², at 10 000 cd m⁻²; ^{c)}At 100 cd m⁻².

4. Conclusions

In conclusion, we synthesized two compounds with electron-withdrawing pyridine and rigid twisted spirobifluorene moiety, 3-4PySF and 4-4PySF. The structural difference between 3-4PySF and 4-4PySF is the position of substituted pyridine rings. Through a series of characterizations, the effect of nitrogen atom positon on the photophysical properties, energy levels, thermal properties, electron-transporting properties and device performances was demonstrated. It was found that the electron-transporting ability of materials could be adjusted according to substitution position of nitrogen atom in the pyridine. The difference in the T_m of 3-4PySF and 4-4PySF suggested that the difference in electrical properties may be due to the different intermolecular interaction in the film state. Green PhOLEDs with 3-4PySF and 4-4PySF as ETM were fabricated, which exhibited a maximum EQE of 20.5% and a lowest turn-on voltage of 2.6 V, superior to TPBi-based comparison device. These results manifest that the integration of pyridine and spirobifluorene is a promising way to design an ideal ETM.

Conflicts of interest

There is no conflict to declare.

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Highlights

- Design and synthesis of two oligopyridine derivatives with different nitrogen positions.
- Adjusting the electron-transporting ability of materials by changing the substitution positon of pyridine.
- High external quantum efficiency over 20% in the green phosphorescent organic light-emitting diodes.