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Novel phosphine oxide-based electron-transporting materials for efficient phosphorescent organic light-emitting diodes

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Three phosphoryl quinoline derivatives, (2,4-diphenylquinolin-3-yl)diphenylphosphine oxide (QDPO), (2,4-diphenylbenzo[h]quinolin-3-yl)diphenylphosphine oxide (B-QDPO) and (2-([1,1'-biphenyl]-4-yl)-4-phenylquinolin-3-yl)diphenylphosphine oxide (**BP-ODPO**), comprising two electron-transport moieties of nitrogen heterocycle and phosphoryl (P=O) group, have been designed and synthesized. All materials exhibit suitable LUMO (lowest unoccupied molecular orbital) /HOMO (highest occupied molecular orbital) levels, large triplet energy gap ($E_T > 3.1$ eV) and excellent thermal stability. These materials were utilized as electron transporting materials for fabricating green phosphorescent organic light-emitting diodes with the configuration of indium tin oxide (ITO)/ MoO₃ (5 nm)/ TAPC (di-[4-(*N*,*N*-ditolyl-amino)-phenyl]cyclohexane) (30 nm)/Ir(tfmppy)₂tpip $(bis(4-trifluoromethylphenylpyridine-N, C^2))$ iridium(tetraphenylimido- diphosphinate) (8) wt%) : mCP [1,3-bis(N-carbazolyl)benzene] (10 nm)/ QDPO or B-QDPO or BP-QDPO (30 nm)/ LiF (1 nm)/ Al (100 nm). These devices exhibited decent performances with peak current efficiency above 80 cd A⁻¹ and external quantum efficiency above 20% as well as negligible efficiency roll-off.

Introduction

Organic light-emitting diodes (OLEDs) have drawn great attention because of their outstanding performances for application in the next generation display technology and lighting.¹ Because phosphorescence complexes can harvest both singlet and triplet excitons, their external/internal quantum efficiencies are four times as high as those of conventional fluorescence materials.² Therefore, the phosphorescent OLEDs (PhOLEDs) are the best choice for practical application. Furthermore, high-efficiency OLEDs with a low driving voltage and simplified device structure are very important for their commercial application. As we know, recombination of holes and electrons within the emitting layer results in the generation of illumination in OLEDs. Consequently, the efficiency of the conversion from electricity to light of an OLED depends greatly upon the effective recombination of holes and electrons in the emitting layer (EML). A balanced charge carrier recombination would benefit for reaching the highest efficiencies. So the ingenious selection of materials for each layer is of vital importance in the design of an exceptionally high-efficient PhOLEDs. In particular, in most OLEDs, because the hole mobility of the hole transport layer is higher than the electron mobility of the electron transport layer,³ the performances of PhOLEDs rely on the capability of electron transport. In light of this, electron-transport materials (ETMs) with excellent electron-transport property, proper singlet and triplet energy gaps and high thermal stability are in high demand.

In the last decade, numerous ETMs with different structural

features have been designed and synthesized for improving OLED performances. A variety of electron-deficient heteroaromatics like pyridine,⁴ triazole,⁵ oxadiazole,⁶ triazine,⁷ phenanthroline,⁸ etc. were chosen as the structural moieties of ETMs. However, as the π -systems extend, the energy gap and triplet energy decrease. In general, because of the long lifetime, the triplet exciton of an EML material (dopant or host) exhibits a long diffusion length to the adjacent layers compared with that of the singlet exciton. Therefore, it is important that the ETMs have a triplet energy gap $(E_{\rm T})$ large enough to prevent diffusion of the triplet exciton from the EML to the electron-transporting layer (ETL). In recent years, phenylphosphine oxide (P=O) derivatives were found to be able to improve the electron mobility of the guest materials such as phosphorescent metal complexes like efficient iridium(III) complex Ir(tfmppy)₂tpip (bis(4-trifluoromethylphenylpyridine- N, C^2))iridium(tetraphenyli midodiphosphinate) reported by our group9 and host materials.10 Unlike other functional group, P=O does not extend the conjugated systems because this unit disturbs the conjugated connection with the core.

In this report, we synthesized and investigated three new phosphoryl quinoline derivatives, **QDPO**, **B-QDPO**, and **BP-QDPO** using simple starting materials and convenient reaction conditions (Scheme 1), which will reduce the manufacturing cost and promote the commercial application of OLEDs. Thereafter, these three phosphoryl compounds were used as electron-transporting/exciton-blocking materials for green phosphorescent OLEDs. All devices exhibited low driving voltages, high efficiency and negligible roll-off.



Scheme 1 Synthetic route to the three new electron-transporting materials (ETMs).

Results and discussion

Synthesis

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The synthetic routes and chemical structures of QDPO, B-ODPO and BP-ODPO were demonstrated in Scheme 1. Amine, aldehyde and alkyne, like "bread and butters" serving as the most basic components, through copper-catalyzed 3A-coupling afforded the propargylamine intermediates 1a, 1b and 1c.¹¹ Then the three target compounds QDPO, B-QDPO and BP-QDPO were prepared via a photocatalyzed radical cascade reaction using very mild reaction conditions (room temperature, green character of light) and very simple and cheap raw materials (amines, aldehydes and alkynes), which would reduce energy consumption and cut cost of raw materials for promoting industrialization of OLEDs. These new compounds were characterized by ¹H NMR, ¹³C NMR and ³¹P NMR spectroscopy and high resolution mass spectrometry (HRMS), respectively. Furthermore, all the materials were further purified by vacuum sublimation before device fabrication.

Thermal stability



Fig. 1 TGA thermogram curves of the compounds.

The stability of the ETMs is of great importance for fabricating stable PhOLEDs. The thermal properties of QDPO, B-QDPO and BP-QDPO were characterized by thermogravimetric analysis (TGA, Fig. 1) and differential scanning calorimetry (DSC, Fig. S1). All the compounds exhibit high thermal tolerance and the decomposition temperatures (T_d) (5% weight loss) are 370, 351 and 342 °C for ODPO, B-ODPO and BP-QDPO, respectively. From the DSC curves it can be calculated that their corresponding melting points are high of 234, 254 and 288 °C, respectively (Fig. S1). The glass transition temperatures (T_{g}) of **QDPO** and **B-QDPO** were 109 and 132 °C, respectively, but that of BP-QDPO was not observed from the DSC curves. These results revealed that the three ETMs can form thermally durable and morphologically stable amorphous thin films, which is important for fabricating high quality OLEDs during thermal evaporation.

Photophysical and electrochemical property



Fig. 2 UV-vis and PL spectra of QDPO, B-QDPO and BP-QDPO in CH_2Cl_2 at room temperature.

Fig. 2 shows the absorption and emission spectra of **QDPO**, **B-QDPO** and **BP-QDPO** in CH_2Cl_2 solution at room temperature. The detailed photophysical data are summarized in Table 1. All compounds exhibit strong absorption bands around Published on 27 July 2017. Downloaded by Newcastle University on 27/07/2017 23:41:24

250 nm in a dichloromethane solution, which may be assigned to the π - π * transition of the nitrogen heterocycle ring. The absorption bands at around 280 nm correspond to the π - π * transitions of benzene rings. The fluorescence emission peaks of three compounds are observed at 405, 406 and 407 nm, respectively. The low temperature photoluminescence spectra at 77 K indicate the triplet energies of **QDPO**, **B-QDPO** and **BP-QDPO** are 3.22, 3.14 and 3.16 eV, respectively, from their phosphorescent peaks (Fig. S2).

The highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of three materials are important for the design of the device structure. To calculate the HOMO and LUMO levels of **QDPO**, **B-QDPO** and **BP-QDPO**, cyclic voltammetry experiments were carried out using ferrocene as the internal standard (Fig. 3). The HOMO levels of **QDPO**, **B-QDPO** and **BP-QDPO** were found to be -6.36, -6.19 and -6.11 eV, respectively, with regard to the energy level of the ferrocene reference (4.8 eV below the vacuum level). The LUMO levels of **QDPO**, **B-QDPO** and **BP-QDPO** were estimated as -2.82, -2.92 and -2.64 eV using the HOMO levels and UV-vis absorption spectra. The suitable LUMO level will

contribute to electron injection and the lower HOMO level benefits for holes/excitons blocking.



Fig. 3 Cyclovoltammety (CV) diagrams of QDPO, B-QDPO and BP-QDPO in acetonitrile.

Compound	$T_{\rm g}/T_{\rm m}/T_{\rm d}^{\rm a)}$	λ_{abs}^{b}	$\lambda_{\rm em}^{\rm b)}$	$E_{\rm T}^{\rm c)}$	$E_{\rm g}^{~\rm d)}$	HOMO/LUMO ^{d)}
	[°C]	[nm]	[nm]	[eV]	[eV]	[eV]
QDPO	109/234/370	245/345	405	3.22	3.54	-6.36/-2.82
B-QDPO	132/254/351	256/280/373	406	3.14	3.27	-6.19/-2.92
BP-QDPO	/288/342	246/287/347	407	3.16	3.47	-6.11/-2.64

^{a)} $T_g/T_m/T_d$: glass transition temperature, melting point and decomposition temperature; ^{b)} Measured at RT in CH₂Cl₂ (10⁻⁵ M); ^{c)} E_T (triplet energy): estimated from the highest-energy peaks of the 77 K phosphorescence spectra in CH₂Cl₂ (10⁻⁵ M); ^{d)} HOMO/LUMO energy levels calculated using the cyclic voltammetry (CV) diagram with ferrocene as the internal standard and the absorption spectra for E_g .

OLEDs performance



Fig. 4 Energy level diagrams of green PHOLEDs and molecular structures of materials used in this study.

To assess the performances of **QDPO**, **B-QDPO** and **BP-QDPO** as the ETMs, typical OLED devices were fabricated using widely reported materials with the configuration of indium tin oxide (ITO)/MoO₃ (5 nm)/TAPC (di-[4-(N,N-ditolyl-amino))

phenyl]cyclohexane) (30 nm) /Ir(tfmppy)₂tpip (8 wt%) : mCP [1,3-bis(N-carbazolyl)benzene] (10 nm) /**QDPO** or **B-QDPO** or **BP-QDPO** or TPBi (2,2',2"-(1,3,5-benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole), 30 nm) /LiF (1 nm)/Al (100 nm). These devices were named as D-QDPO, D-B-QDPO, D-BP-QDPO and D-TPBi, respectively. MoO₃ and LiF served as hole- and electron-injecting interface modified materials, respectively. TAPC and mCP acted as hole-transporting and host materials, respectively. The widely used electron transport material TPBi was chosen as a reference to evaluate three synthesized materials. The chemical structures of the used materials as well as the energy level diagram of the device architecture were illustrated in Fig. 4 and Fig S4.

The EL spectra, current density – voltage – luminance (J - V - L), current efficiency - luminance $(\eta_c - L)$ and power efficiency - luminance $(\eta_p - L)$ curves of the devices are presented in Fig 5 and the EL data are summarized in Table 2. The electroluminescence spectra of these devices reveal the emission maxima at 523 nm corresponding to the PL of Ir(tfmppy)₂tpip with Commission Internationale de l'Éclairage (CIE) color coordinates of (0.32, 0.64),^{9(a)} and no emission from host and adjacent materials (Fig. 5(a)) These results indicate that the

recombination of the carriers (holes and electrons) occurs in the EML completely, and the excitons formed are well confined within the EML. All devices exhibit a low turn-on voltage of 2.9 V, which is possibly due to the optimal LUMO levels and high electron mobility of ODPO, B-ODPO and BP-ODPO. Furthermore, excellent EL performances with the maximum luminance close to 40 000 cd/m^2 , the peak current efficiency $(\eta_{c max})$ of 83.53 cd A⁻¹, maximum external quantum efficiency (EQE_{max}) of 21.9% and peak power efficiency ($\eta_{p,max}$) of 67.27 Im W⁻¹ were achieved by device D-QDPO. These performances are higher than those of other two devices. D-B-QDPO showed a $\eta_{\rm c,max}$ of 77.85 cd A⁻¹, EQE_{max} of 20.4% and with a higher $\eta_{\rm p,max}$ of 70.45 lm W⁻¹, while D-BP-QDPO exhibited a $\eta_{c,max}$ of 62.72 cd A⁻¹, EQE_{max} of 16.4% and a $\eta_{p,max}$ of 53.16 lm W⁻¹. By comparison, the EL performances of D-QDPO and D-B-QDPO are better than that of D-TPBi, which shows lower maximum

efficiency of 64.00 cd A⁻¹ and 49.07 lm W⁻¹, and a little higher turn-on voltage of 3.1 V (Table 2, Fig. S3 (b) and (c)). Though electron-only devices (EODs) exhibit a little higher electron-current density of TPBi than that of three new materials (Fig. S3(a)), **QDPO**, **B-QDPO**, **BP-QDPO** own lower LUMO levels than that of TPBi (Fig. 4), which will reduce electron injection barrier and contribute to the electron injection and transport for promoting the balanced recombination of electrons and holes as well as leading to the suppressed current leakage for achieving high efficiency. Besides, the deeper HOMO levels of QDPO, B-QDPO, BP-QDPO benefit for holes/excitons blocking, and the large triplet energy gap ($E_T > 3.0$ eV) would also prevent diffusion of the triplet excitons from the EML to the electron-transporting layer (ETL) for improving the utilization rate of excitons.



Fig. 5 (a) EL spectra at 50 mA; (b) Current density and luminance versus voltage; (c) Current efficiency versus luminance; (d) Power efficiency versus luminance.

Table 2 Key EL Data of the OLEDS.									
Device	$V_{turn-on}^{a)}$ [V]	$L_{\rm max}({\rm voltage})^{\rm b)}$ [cd m ⁻² (V)]	$\eta_{c.max}^{c)}$ [cd A ⁻¹]	$\eta_{c,100/1000}^{d)}$ [cd A ⁻¹]	$\eta_{\mathrm{p.max}}^{\mathrm{e})}$ [lm W ⁻¹]	$EQE_{\max,100,1000}^{\text{f}}$ [%]			
D-QDPO	2.9	38 929(13.5)	83.53	79.36/82.42	67.27	21.9/20.8/21.6			
D-B-QDPO	2.9	39 311(13.0)	77.85	76.29/73.42	70.45	20.4/20.0/19.2			
D-BP-QDPO	2.9	38 600(12.3)	62.72	55.66/55.11	53.16	16.4/14.6/14.4			
D-TPBi	3.1	40 422(13.3)	64.00	60.13/62.70	49.07	16.7/15.7/16.3			

^{a)} $V_{turn-on}$: turn-on voltage recorded at a brightness of 1 cd m⁻²; ^{b)} L_{max} : maximum luminance; ^{c)} $\eta_{c,max}$: maximum current efficiency; ^{d)}current efficiencies measured at the brightness of 100 cd m⁻²; ^{a)} $\eta_{p,max}$: maximum power efficiency; ^{f)} $EQE_{max, 100, 1000}$: maximum external quantum efficiency, external quantum efficiency at 100 cd m⁻² and 1 000 cd m⁻².

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In general, phosphorescent OLEDs exhibit severe roll-off at a higher current density due to triplet-triplet annihilation. Noticeably, with increase of the current density, the device D-QDPO exhibits very small efficiency roll-off ratios with the η_c of 79.36 and 82.42 cd A⁻¹ at practical brightness of 100 and 1 000 cd m⁻², respectively, as well as EQE of 20.8% and 21.6% without any light-outcoupling enhancement. Their outstanding EL performances of QDPO-based device may be attributed to the following facts: 1) the nitrogen-containing heterocycle would be helpful for electron transporting; 2) the suitable LUMO level will contribute to electron injection and the lower HOMO level benefits for holes/excitons blocking. Therefore, a better balanced charge injection and transport will promote the recombination of electrons and holes and broaden the recombination zone, as well as lead to the suppressed current leakage in the devices. Taking those facts into account, high efficiency and small efficiency roll off could be achieved by QDOP-based device.

Conclusions

In conclusion, three new ETMs with phosphoryl (P=O) moiety and nitrogen heterocycle ring exhibit suitable LUMO/HOMO levels, large triplet energy gap (E_T) and excellent thermal stability. These materials were then utilized as electron transporting materials for fabricating green phosphorescent OLEDs. The devices exhibited decent performances with peak current efficiency above 80 cd A⁻¹ and external quantum efficiency above 20% as well as negligible efficiency roll-off. Further materials screening and device optimization of phosphorylated quinolines as ETMs for OLEDs are underway.

Experimental section

Materials and measurements

Commercially available reagents were used as received without purification. Raw Materials were purchased from Sigma-Aldrich. Column chromatography was carried out on silica gel (300-400 mesh). Analytical thin-layer chromatography was performed on glass plates of Silica Gel GF-254 with detection by UV. ¹H, ¹³C and ³¹P NMR spectra were recorded on a Bruker AVANCE 400M spectrometer. The chemical shift references were as follows: ¹H NMR (CDCl₃) 7.26 ppm; ¹³C NMR (CDCl₃) 77.00 ppm. HRMS spectra were carried out on Micromass GCT (ESI). Absorption and photoluminescence spectra were measured on a UV-3100 spectrophotometer and a Hitachi F-4600 photoluminescence spectrophotometer, respectively. Cyclic voltammetry measurements were conducted on a MPI-A multifunctional electrochemical and chemiluminescent system (Xi'an Remex Analytical Instrument Ltd. Co., China) at room temperature, with a polished Pt plate as the working electrode, platinum thread as the counter electrode and Ag-AgNO₃ (0.1 M) in CH₃CN as the reference electrode, tetra-n-butylammonium perchlorate (0.1 M) was used as the supporting electrolyte, using Fc^+/Fc as the internal standard, the scan rate was 0.1 V/s.

OLEDs fabrication and measurement

Indium-tin-oxide (ITO) coated glass with a sheet resistance of 10 Ω sq⁻¹ was used as the anode substrate. Prior to film deposition,

patterned ITO substrates were cleaned with detergent, rinsed in de-ionized water, dried in an oven, and finally treated with oxygen plasma for 5 minutes at a pressure of 10 Pa to enhance the surface work function of ITO anode (from 4.7 to 5.1 eV). All the organic layers were deposited with the rate of 0.1 nm s⁻¹ under high vacuum ($\leq 2 \times 10^{-5}$ Pa). The doped layers were prepared by co-evaporating dopant and host material from two individual sources, and the doping concentrations were modulated by controlling the evaporation rate of dopant. MoO₃, LiF and Al were deposited in another vacuum chamber (\leq 8.0×10^{-5} Pa) with the rates of 0.01, 0.01 and 1 nm s⁻¹, respectively. The thicknesses of these deposited layers and the evaporation rate of individual materials were monitored in vacuum with quartz crystal monitors. A shadow mask was used to define the cathode and to make ten emitting dots (with the active area of 10 mm²) on each substrate. Device performances were measured by using a programmable Keithley source measurement unit (Keithley 2400 and Keithley 2000) with a silicon photodiode. The EL spectra were measured with a calibrated Hitachi F-7000 fluorescence spectrophotometer. Based on the uncorrected EL fluorescence spectra, the Commission Internationale de l'Eclairage (CIE) coordinates were calculated using the test program of Spectrascan PR650 spectrophotometer. The EQE of EL devices were calculated based on the photo energy measured by the photodiode, the EL spectrum, and the current pass through the device.

General procedure for the preparation of phosphorylated quinolones (QDPO, B-QDPO and BP-QDPO).

Propargylamines (1a, 1b, 1c) were prepared according to the previous publications.¹¹ A dry and argon-flushed *Schlenk*-flask, equipped with a magnetic stirring bar was charged with propargylamine (0.3 mmol), diphenylphosphine oxide (0.6 mmol), $Ir(ppy)_3$ (0.009 mmol), iodobenzene diacetate (0.6 mmol), sodium bicarbonate (0.45 mmol). Then dry DMF (3.0 mL) was added and the reaction mixture was irradiated with a green LED lamp (5 W). After stirring for 36 h at room temperature, the crude mixture was purified by flash column chromatography to afford the target product **QDPO**, **B-QDPO** and **BP-QDPO** with the yields of 78%, 60% and 61%, respectively.

(2,4-diphenylquinolin-3-yl)diphenylphosphine oxide (QDPO): White solid. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, J = 8.2 Hz, 1H), 7.81 (t, J = 7.4 Hz, 1H), 7.71 (d, J = 4.3 Hz, 3H), 7.52 – 7.44 (m, 1H), 7.30 – 7.19 (m, 7H), 7.15 – 7.05 (m, 7H), 6.98 (d, J = 4.7 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 162.98 (d, J = 11.3 Hz), 158.24 (s), 147.85 (s), 141.90 (s), 136.08 (s), 135.72 (d, J = 6.0 Hz), 135.03 (s), 132.22 (s), 131.53 (s), 130.62 – 130.08 (m), 129.84 (d, J = 2.6 Hz), 129.59 (s), 129.21 (s), 128.51 (d, J = 5.7 Hz), 128.18 (s), 127.68 (dd, J = 21.4, 9.1 Hz), 126.79 (d, J = 20.4 Hz), 126.65 – 126.58 (m), 125.68 – 125.25 (m), 124.57 (s), 113.94 (s). ³¹P NMR (162 MHz, CDCl₃) δ 19.98. HRMS (ESI) m/z calcd for C₃₃H₂₄NOPH [M+H]: 482.1674, found: 482.1671.

(2,4-diphenylbenzo[*h*]quinolin-3-yl)diphenylphosphine oxide (B-QDPO): White solid. ¹H NMR (400 MHz, CDCl₃) δ 9.51 – 9.30 (m, 1H), 8.00 – 7.83 (m, 3H), 7.79 – 7.64 (m, 3H), 7.55 (d, J = 9.2 Hz, 1H), 7.26 (dd, J = 14.3, 5.3 Hz, 6H), 7.16 (dt, J = 23.8, 7.4 Hz, 6H), 7.06 (t, J = 7.2 Hz, 2H), 7.01 – 6.91 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 162.17 (d, J = 11.0 Hz), 157.04 (d, J = 9.1 Hz), 146.63 (s), 142.34 (s), 136.44 – 135.94 (m), 135.19 (s), 134.24 (s), 132.44 (s), 131.04 (d, J = 10.6 Hz), 130.35 (d, J = 8.7 Hz), 129.80 (d, J = 2.4 Hz), 129.27 (s), 128.65 (s), 128.32 (s), 127.61 (dd, J = 17.2, 13.7 Hz), 127.23 (s), 125.61 (d, J = 14.2 Hz), 124.54 (s), 123.08 – 122.66 (m). ³¹P NMR (162 MHz, CDCl₃) δ 20.32. HRMS (ESI) *m/z* calcd for C₃₇H₂₆NOPH [M+H]: 532.1830, found: 532.1829.

(2-([1,1'-biphenyl]-4-yl)-4-phenylquinolin-3-yl)diphenylphosp hine oxide (BP-QDPO): White solid. ¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, J = 8.2 Hz, 1H), 7.88 – 7.67 (m, 4H), 7.54 – 7.41 (m, 5H), 7.36 – 7.23 (m, 9H), 7.20 (d, J = 6.9 Hz, 1H), 7.16 – 7.04 (m, 4H), 6.98 (d, J = 4.8 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 162.63 (d, J = 11.1 Hz), 158.18 (d, J = 8.7 Hz), 147.95 (s), 141.19 (s), 140.92 (s), 136.06 (s), 135.69 (d, J = 6.1 Hz), 135.01 (s), 132.24 (s), 131.58 (s), 130.83 (s), 130.39 (d, J = 8.7 Hz), 129.87 (d, J = 2.5 Hz), 129.62 (s), 128.76 (s), 128.56 (s), 127.55 (dd, J = 27.3, 14.5 Hz), 127.25 – 126.54 (m), 125.81 – 125.33 (m), 124.69 (s). ³¹P NMR (162 MHz, CDCl₃) δ 20.03. HRMS (ESI) *m/z* calcd for C₃₉H₂₈NOPNa [M+Na]: 580.1806, found: 580.1803.

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Graphical abstract



Three electron transporting materials comprising nitrogen heterocycle and phosphoryl moiety were utilized for green PhOLEDs, which exhibited decent performances with peak current efficiency above 80 cd A^{-1} and external quantum efficiency above 20% as well as negligible efficiency roll-off.