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Synthesis and properties of n-type triphenylpyridine derivatives and applications in deep-blue organic light-emitting devices as electron-transporting layer[†]

Na Li,^a Shiu-Lun Lai,^b Weimin Liu,^a Pengfei Wang,^{*a} Juanjuan You,^a Chun-Sing Lee^{*b} and Zengtao Liu^b

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Two series of n-type triphenylpyridine derivatives with good thermal properties and efficient deep-blue emissions were designed, synthesized and systematically characterized. Most of them show high glass transition temperatures ($T_g > 100$ °C), relatively high electron mobilities, large ionization potentials (IP > 6.31 eV) and suitable electron affinities (EA > 2.93 eV) for facilitating efficient electron-injection. These attributes of the n-type triphenylpyridine derivatives favours their applications in organic light-emitting devices (OLEDs) as electron-transporting and hole-blocking materials (ETMs and HBMs). With these new materials, deep-blue OLEDs with a configuration of indium-tin oxide (ITO)/ α -napthylphenylbiphenyl diamine (NPB)/9,10-di(2-naphthyl)anthracene (ADN)/triphenylpyridine derivatives as ETMs and HBMs. The devices show higher efficiency (2.54 cd A⁻¹), and better color purity (0.15, 0.10) compared to those of similarly-structured blue OLEDs using state-of-the-art ETMs. The large *IP* and deep-blue emission of the triphenylpyridine derivatives are considered to be key factors for the higher efficiencies and better color purity. Optical and other properties of the compounds are discussed in terms of their molecular structures.

1. Introduction

Organic light-emitting device (OLED) has been considered as a promising technology because of its high efficiency, wide viewing angle, low cost and many other merits.¹⁻³ Considerable progress has been made recently in flat panel displays (FPDs) based on OLEDs. In the past two decades, various approaches have been attempted to enhance performance of OLEDs.⁴⁻⁶ For instance, chemists have designed and synthesized a large number of organic materials to meet various needs for different functional requirements.^{7,8} A classical example is the use of different organic materials in a device to function respectively as the lightemitting layer (EML), the electron-transporting layer (ETL) and the hole-transporting layer (HTL).^{9,10} Compared to the emitting materials (EMs) and the hole-transporting materials (HTMs),

the development of electron-transporting materials (ETMs) is lagging behind. It is thus important to design and synthesize ETMs with improved performance.^{11,12} A good ETM should satisfy three essential requirements:¹³ (i) high electron mobility is an important attribute of an ETM. It is well-known that holemobilities of many HTMs are several orders of magnitude higher than the electron-mobilities of commonly used ETMs.14 As a result, in many devices, the hole-electron recombination would occur near the cathode instead of the middle of the EML. This can affect the color purity as well as decrease the current efficiency. (ii) An ETM should have a suitable electron affinity (EA) and a large ionization potential (IP). A suitable EA can minimize the electron-injection barrier and thus the turn-on/operating voltages; meanwhile a large IP can effectively block the hole from entering the ETL. In fact, in many device structures, good electron-transporting and hole-blocking properties are simultaneously required.¹⁴ (iii) A good ETM should also have a high glass transition temperature (T_{o}) and good thermal stability for ensuring good operational stability.

From the viewpoint of molecular design, n-type molecules with electron deficient π -systems are generally considered to have high electron mobilities. Typical examples include metalloles, oxadiazoles, pyridines, fluorinated aromatics *etc.* Among these, pyridine derivatives have attracted much attention.¹⁵ In this work, we designed and synthesized two groups of n-type materials based on triphenylpyridine derivatives for applications

^aKey Laboratory of Photochemical Conversion and Optoelectronic Materials Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beiyitiao No. 2, Zhongguancun, Haidian District, Beijing, P. R. China. E-mail: wangpf@mail.ipc.ac.cn; Fax: (+86) 10-8254-3512

^bCenter of Super-Diamond and Advanced Films (COSDAF), Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong SAR, P. R. China. E-mail: apcslee@cityu. edu.hk

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as ETMs with hole-blocking ability in deep-blue OLEDs. These triphenylpyridine derivatives are divided into two groups for comparison: Group A: 2,4-diphenyl-6-p-tolylnicotinonitrile (DPTNT), 4,4'-(1,4-phenylene) bis(2-phenyl-6-p-tolylnicotinonitrile) (p-PPtNT),¹⁶ 4,4'-(1,3-phenylene) bis(2-phenyl-6-p-tol-(*m*-PPtNT) vlnicotinonitrile) and 4,4'-(1,3-phenylene)bis(6-(4-methoxyphenyl)-2-phenylnicotinonitrile) (m-PmPNT); and Group B: 4-(4-cvanophenvl)-2.6-diphenvlnicotinonitrile (CPPNN), 6,6'-(1,4- phenylene) bis(2-phenyl-4-p-tolylnicotinonitrile) (p-PPtNN),¹⁶ 6,6'-(1,3-phenylene) bis(2-phenyl-4-p-tolylnicotinonitrile) (m-PPtNN) and 6,6'-(1,3-phenylene) bis (4-(4-*tert*-butylphenyl)-2-phenylnicotinonitrile) (m-PbPNN) (Scheme 1). Synthesis procedures of these compounds are similar to those described in literatures.¹⁷ Most of these compounds were found to have high glass transition temperatures ($T_{o} > 100 \,^{\circ}\text{C}$), relatively high electron mobilities (in the order of 10^{-5} cm² V⁻¹ s^{-1}), large ionization potentials (*IP* > 6.31 eV) and suitable electron affinities (EA > 2.93 eV). High performances are realized for the ADN based deep-blue OLEDs with these compounds as ETMs and HBLs. Differences in electroluminescent (EL) properties of the compounds are discussed in terms of their molecular structures.

2. Results and discussion

2.1 Thermal stability

Fig. 1 shows thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements of the two groups of



Scheme 1 The molecular structures of the two groups of triphenylpyridine derivatives.



Fig. 1 TGA and DSC data of the triphenylpyridine derivatives a) TGA of Group A; b) DSC of Group A; c) TGA of Group B; d) DSC of Group B).

triphenylpyridine derivatives. T_d is defined as the temperature at which 5% weight loss occurs during heating. Except DPTNT and CPPNN, all the other compounds are thermally stable up to 370 °C (Fig. 1(a) & (c) and Table 1). The higher T_d are beneficial to the thermal stability of these materials in OLED applications. T_g and T_m values obtained from DSC measurements (Fig. 1(b) & (d)) are tabulated in Table 1. The T_m values for *p*-PPtNT,

m-PPtNT, m-PmPNT, p-PPtNN and m-PPtNN are in the range of 308~363 °C, while the T_g values for p-PPtNT, m-PPtNT, m-PmPNT, p-PPtNN and m-PbPNN are in the range of 101.5~138.7 °C. Comparing to a commonly used ETM with low T_{g} (60 °C), 4,7-diphenyl-1,10-phenanthroline (BPhen), with the highest T_{g} of the five triphenylpyridine derivatives, allows a wider range of applications in various organic electronic devices. The differences in $T_{\rm d}$, $T_{\rm m}$ and $T_{\rm g}$ values of the two groups of compounds can be attributed to their different structures. The molecule with para molecular orientation framework is proved to have a bulky structure and higher polarity than that with meta molecular orientation framework, which can increase the thermal stability of the para molecular orientation framework. This explains the highest temperature parameters of p-PPtNT among all Group A molecules. For m-PPtNT and *m*-PmPNT of Group A, the methoxyl group in *m*-PmPNT can increase the molecular polarity by a larger extent than the methyl group of *m*-PPtNT. Comparing with the above-mentioned three compounds, DPTNT has relatively lower thermal parameters due to its smaller molecular size and weight. So the T_d , T_m and T_g values of Group A compounds are in the order of p-PPtNT > *m*-PmPNT > *m*-PPtNT > DPTNT. For Group B compounds, p-PPtNN with para molecular orientation framework has the highest $T_{\rm d}$ and $T_{\rm m}$, while $T_{\rm g}$ of *m*-PbPNN (138.7 °C) is higher than that of p-PPtNN (101.5 °C) because the tert-butyl group in *m*-PbPNN can increase T_g more than methyl group in *p*-PPtNN.

2.2 IP and EA characterization

The IP and EA values of the two groups of triphenylpyridine derivatives are also listed in Table 1. Phenylpyridine moiety has been shown to contribute to good electron-transporting ability and large IP for hole-blocking ability.18-20 It was found that the IP of DPTNT (7.05 eV) and p-PPtNT (6.81 eV) of Group A and CPPNN (7.10 ev), p-PPtNN (6.87 eV), m-PPtNN (6.93 eV) and m-PbPNN (6.90 eV) of Group B are all larger than those of typical hole-blockers, such as, 2,9-dimethyl-4,7-diphenylphenathroline (BCP, IP = 6.70 eV),²¹ 1,3,5-tris (phenyl-2-benzimidazolyl) benzene (TPBI, IP = 6.70 eV),²² BPhen (IP = 6.40 eV)²³ and another new electron-transporting material reported by Kido et al. $(IP = 6.67 \text{ eV}).^{24}$ In general, a para molecular orientation framework would give a more extended π -conjugation comparing to a corresponding meta orientation. These would generally result in deeper highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital

(LUMO) energy levels (i.e. larger in numerical values). At the same time, electron-withdrawing (donating) groups linked to the benzene ring can also lower (raise) the HOMO and LUMO levels. These explain why the IPs of the compounds of Group A are in the order of *p*-PPtNT > *m*-PmPNT. *EA* values for them are in the same order. Their EA values $(3.57 \sim 2.20 \text{ eV})$ are suitable for minimizing the electron-injection barrier and thus the turn-on/operating voltages. DPTNT has larger HOMO and LUMO values mainly because of its asymmetric molecular structure which has shorter π -conjugation length than the other three triphenylpyridine derivatives with symmetric molecular structures. From Table 1, it can be found that the corresponding IP and EA values of p-PPtNN, m-PPtNN, and m-PbPNN of Group B are almost the same. They are slightly larger than those of Group A. It is considered that the sp-hybrid cyano group in the para orientation in Group B has a higher electron withdrawing ability and thus lowers the energy levels.

2.3 Electron mobility

The electron mobilities of the two groups of triphenylpyridine derivatives were investigated by transient electroluminescence (EL) method.²⁵ Table 2 and Figure S1[†] show that electron mobilities of all the triphenylpyridine derivatives are in the order of 10^{-5} cm²/Vs, which are one order of magnitude higher than that of Alq3,²⁶ two orders of magnitude higher than that of BCP27 and comparable to that of TPBI.28 Their relatively high electron mobilities are beneficial for achieving low driving voltage and high efficiency. The compounds with meta molecule orientation were observed to have higher electron mobilities than those with *para* molecular orientation (e.g. m-PPtNT > p-PPtNT, m-PPtNN > p-PPtNN). This can also be attributed to the bulky structures of compounds with para molecule orientation, which leads to more steric hindrance that makes packing or aggregating of molecules more difficult. For the same molecule orientation, compounds from Group A exhibit slightly higher mobilities than those from Group B (e.g. p-PPtNT > p-PPtNN and m-PPtNT > m-PPtNN). This might be caused by the fact that the cyano groups in Group B compounds reduce the molecular planarity and thus the mobility.

2.4 Absorption and emission spectroscopy

Absorption and fluorescent spectral data of the two groups of triphenylpyridine derivatives in different solvents at room

 Table 1
 Summary of thermal and spectral data of the two groups of triphenylpyridine derivatives

Compound	$T_{\rm d}/T_{\rm m}/T_{\rm g} [^{\circ}{\rm C}]$	IP/EA [eV]	$\lambda^{ab.}_{max.}^{a}$ [nm]	$\lambda^{\text{em.}}_{\text{max.}}{}^{b}$ [nm]	$E_{\mathrm{T}}{}^{c}$ [eV]
DPTNT	250/177/46.6	7.05/3.63	281/335	380	3.07
<i>p</i> -PPtNT	388/363/138.5	6.81/3.57	294/330	407	3.04
<i>m</i> -PPtNT	372/308/130.2	6.31/2.93	281/337	403	3.14
<i>m</i> -PmPNT	384/313/131.3	5.42/2.20	283/352	421	3.04
CPPNN	278/No T _m & T _g	7.10/3.70	280/333	389/475	2.76
<i>p</i> -PPtNN	375/383/101.5	6.87/3.69	291/355	427	2.99
<i>m</i> -PPtNN	374/317/No T _s	6.93/3.52	280/328	387	2.75
<i>m</i> -PbPNN	374/219/138.7	6.90/3.47	280/328	383	2.77

 $^{a} \lambda^{ab.}_{max.}$: maximum wavelength of absorption (deposited on the quartz substrates). $^{b} \lambda^{em.}_{max.}$: maximum wavelength of emission (vacuum deposited on quartz substrates). $^{c} E_{T}$: triplet energy level (in 2-methyltetrahydrofuran solution at 77 K).

ETMs	Electron mobility cm ² V ⁻¹ s ⁻¹	Electric field $V cm^{-1}$	Reference
DPTNT	$2.8 imes 10^{-5} \sim 3.7 imes 10^{-5}$	$5.6 \times 10^{5} \sim 10 \times 10^{5}$	This work
<i>p</i> -PPtNT	$4.6 imes 10^{-5} \sim 5.6 imes 10^{-5}$	$5.6 \times 10^{5} \sim 10 \times 10^{5}$	This work
<i>m</i> -PPtNT	$9.2 imes 10^{-5} \!\!\sim \!\! 9.9 imes 10^{-5}$	$5.6 \times 10^{5} \sim 10 \times 10^{5}$	This work
<i>m</i> -PmPNT	$5.5 imes 10^{-5} \sim 6.1 imes 10^{-5}$	$5.6 \times 10^{5} \sim 10 \times 10^{5}$	This work
CPPNN	$5.2 imes 10^{-5} \sim 6.3 imes 10^{-5}$	$5.6 \times 10^{5} \sim 10 \times 10^{5}$	This work
<i>p</i> -PPtNN	$2.4 imes 10^{-5} \sim 4.0 imes 10^{-5}$	$5.6 \times 10^{5} \sim 10 \times 10^{5}$	This work
<i>m</i> -PPtNN	$4.4 imes 10^{-5} \sim 4.8 imes 10^{-5}$	$5.6 \times 10^{5} \sim 10 \times 10^{5}$	This work
<i>m</i> -PbPNN	$6.7 imes 10^{-5} \!\!\sim \!\! 8.5 imes 10^{-5}$	$5.6 \times 10^{5} \sim 10 \times 10^{5}$	This work
TPBI	$4.4 imes 10^{-5} \sim 7.1 imes 10^{-5}$	$5.6 \times 10^{5} \sim 10 \times 10^{5}$	This work
TPBI	$3.3 imes 10^{-5} \sim \! 8.0 imes 10^{-5}$	$4.7 \times 10^{5} \sim 7.0 \times 10^{5}$	28
Alq3	$1.4 imes 10^{-6}$	4.0×10^{5}	26
BCP	6.0×10^{-7}	$7.0 imes 10^{\circ}$	27

Table 2 Electron mobilities of triphenylpyridine derivatives measured by transient electroluminescence (EL) method

temperature are listed in Table S1 and corresponding spectra are shown in Figure S2.[†] The two groups of triphenylpyridine derivatives possess a strong absorption band with a maximum at approximately 270 or 280 nm and a shoulder at 310~340 nm. As mentioned, a para molecular orientation framework would give a more extended π -conjugation compared to a corresponding *meta* orientation. These would generally result in longer $\lambda^{ab.}_{max.}$ (wavelength of absorption maximum). So the $\lambda^{ab.}_{max.}$ of *p*-PPtNT and p-PPtNN are the longest. Peak wavelengths of the fluorescent spectra of the eight triphenylpyridine derivatives shown in Table S1 are red-shifted from several nanometres to several tenths of nanometres with increasing solvent polarity.[†] Moreover, $\varphi_{\rm em}$ (emission quantum yield) for all the compounds increase with increasing solvent polarity from non-polar to moderately polar solvents, then decrease with further increase of solvent polarity. This indicates the co-existence of both "negative" and "positive" solvatokinetic effects. The negative solvatokinetic effect may be attributed to "proximity effects"; whereas, the positive solvatokinetic effect may be caused by the interaction between the molecule and the surrounding polar solvent (acetonitrile & methanol), which can reduce bandgap, and result in more non-radiative decay.

Fig. 2 shows absorption and emission spectra of the two groups of triphenylpyridine derivatives in solid films deposited on quartz substrates. The compounds show two absorption peaks at about 280~294 and 328~355 nm (Fig. 2 and Table 1). They show photoluminescent (PL) peaks in the range of 380 to 427 nm (Fig. 2 and Table 1). Exceptionally, the PL spectrum in solid film for CPPNN has a longer wavelength peaked at 475nm, while only one peak at 400 nm was observed in solution (shown in Figure S1).† It may be attributed to the formation of intermolecular aggregates in solid film, which is often found in a variety of organic films.^{29,30} It is well-known that color purity of deep-blue OLEDs has been a challenge for years, as emissions from other layers besides the EML that often contribute to the electroluminescence. The triphenylpyridine derivatives employed here are expected to improve the color purity of the devices for two reasons. Firstly, their large IPs would effectively block the hole from entering them and lead to a better confinement of the recombination in the EML. On the other hand, as they are deepblue emitters themselves, even if recombination takes place within these ETMs, the emission color will not be severely affected. Hence, these materials with short PL wavelength are suitable for applications as ETMs in deep-blue OLEDs except CPPNN which has another emission peak of longer wavelength at 475 nm.

2.5 Phosphorescence spectroscopy and $E_{\rm T}$

Phosphorescence spectra of the triphenylpyridine derivatives were also measured in 2-methyltetrahydrofuran solutions at 77 K. The $E_{\rm T}$ values of the compounds are in the range of 3.04–3.14 eV (Group A) and 2.75–2.99 eV (Group B) (Fig. 3 and Table 1). The values are larger than those of the most typical phosphorescent emitters, including the blue phosphorescent



Fig. 2 Absorption and fluorescent emission spectra of the two groups of triphenylpyridine derivatives in solid film (deposited on quartz substrates).

material iridium(III) bis[(4,6-difluorophenyl)-pyridinato-N,C2'] picolinate (FIrpic, 2.65 eV) and green phosphorescent material *fac*-tris(2-phenylpyridine) iridium (Ir(PPy)₃, 2.55 eV). The high $E_{\rm T}$ levels can effectively confine the triplet excitons in the phosphorescent emissive layer for application as ETL in phosphorescent OLEDs of blue and other colors. $E_{\rm T}$ values of Group B compounds are slightly smaller than those of Group A compounds. It may be attributed to the lower band gap in Group B compounds as good π -overlap can extend the conjugation length. For Group A compounds, the cyano group is located such that there is a shorter conjugation length. Moreover the location of the cyano in Group A can cause the bridge to twist out of plane due to unfavorable steric interaction thus further shortening the conjugation length resulting in higher $E_{\rm T}$.

2.6 EL Performance

To confirm the electron-transporting and hole-blocking abilities of the triphenylpyridine derivatives, we fabricated devices with a configuration of ITO/NPB [60 nm]/ADN [30 nm]/a triphenylpyridine derivative [30 nm]/LiF [1 nm]/MgAg [100 nm, 10 : 1]. In the device, ITO patterned on glass is used as the anode; NPB is used as the HTL; ADN is used as the blue EML; the two groups of triphenylpyridine derivatives are used as ETLs and holeblocking layers (HBLs); and the LiF/MgAg bilayer is used as a composite cathode.

Fig. 4(a) shows the current density (J)-voltage (V)-luminecence (L) curves of the devices based on the Group A compounds. It can be seen that the turn-on voltages (defined as



Fig. 3 Phosphorescent spectra of the triphenylpyridine derivatives in 2-methyltetrahydrofuran solutions at 77 K.

the voltage required to give a luminance of 1 cd m⁻²) for the devices are 3.5 V (DPTNT), 4.1 V (*p*-PPtNT), 3.5 V (*m*-PPtNT) and 3.9 V (*m*-PmPNT), respectively. The values are all lower than those of the corresponding devices based on Alq3, TPBI and BCP/Alq3.³¹⁻³⁶ The lower turn-on voltages are closely related to their smaller electron-injection barriers, which enable efficient electron-injection from the cathode. Moreover, the sequence of J–V curves for devices respectively based on the four triphenylpyridine derivatives is consistent with that of their L–V curves. In other words, the current density and the luminous are both in the order of DPTNT > *m*-PPtNT > *m*-PbPNT > *p*-PPtNT at the same voltage. The current efficiency (η_L)–current density (*J*)–power efficiency (η_P) characteristics of the four devices are shown in Fig. 4(b). The maximum current efficiencies of devices are 1.51 cd A⁻¹ (DPTNT), 2.54 cd A⁻¹ (*p*-PPtNT),



Fig. 4 EL characteristics of devices based on the triphenylpyridine derivatives of Group A as ETL. Device structure: ITO/NPB [60 nm]/ ADN [30 nm]/a triphenylpyridine derivative [30 nm]/LiF [1 nm]/MgAg [100 nm 10 : 1]. (a): Current density (*J*)–Voltage (*V*)–Luminecence (*L*). (b): Current efficiency (η_L)–*J*–power efficiency (η_P). (c): EL spectra.

2.15 cd A⁻¹ (m-PPtNT) and 2.12 cd A⁻¹ (m-PmPNT), respectively. The results, except that of DPTNT, are considerably higher than those of devices based on Alq3 (1.60 cd A^{-1}), TPBI (1.30 cd A⁻¹) and BCP (as HBL)/Alq3 (1.30 cd A⁻¹) reported previously.³¹⁻³⁶ Power efficiencies of the devices are also higher than corresponding values reported in the literature.^{31–36} On one hand, the high efficiencies for devices based on the present triphenylpyridine derivatives can be attributed to their relatively high electron-transporting ability. On the other hand, these compounds with large IPs can more effectively confine electrons in the EML. This increases the recombination of electron and charge within the EML and thus contributes to the improved efficiency. It is worthy to note that the p-PPtNT based device has a better performance than the *m*-PPtNT based device, though the latter has a higher electron mobility than the former. As p-PPtNT has a lager IP than m-PPtNT, p-PPtNT would better confine the exciton in the EML. These show that performances of the present devices are controlled by both the carrier mobility and hole blocking ability of the ETL. EL spectra of the devices are depicted in Fig. 4(c). EL peak positions (and Commission Internationale de L'Eclairage (CIE) coordinates) of the devices based on DPTNT, p-PPtNT, m-PPtNT and m-PmPNT are 440 nm (0.15, 0.08), 452 nm (0.15, 0.12), 452 nm (0.15, 0.11) and 448 nm (0.15, 0.12), respectively. The deep-blue emission of EL spectra for devices based on the four triphenylpyridine derivatives can be attributed to the emission of ADN. The devices based on these triphenylpyridine derivatives exhibit better color purity than the corresponding devices based on other ETMs reported previously.³¹⁻³⁶ The CIE coordinates are closer to the National Television System Committee (NTSC) standards of (0.14, 0.08)³⁷ for blue emission. The EL spectra for devices based on these triphenylpyridine derivatives manifest these compounds with large IPs confine electrons in the ADN layer triumphantly. The *IP* value of *m*-PmPNT is smaller (5.42 eV); however, the color purity of the device based on *m*-PmPNT is better. Therefore, it can be deduced that the deep-blue emission of m-PmPNT may contribute to the better color purity.

Different EL properties of the Group A compounds can be interpreted in terms of their different *IPs*. As discussed above, the *IPs* of the compounds are in the order of *p*-PtNT > *m*-PtNT > *m*-PmPNT > DPTNT. A larger *IP* value implies a better holeblocking ability which ensures a better confinement of the electron-hole recombination in the EML. This not only enhances the color purity, but also leads to better efficiency as the EML is typically optimized. Thus, among the devices based on these ETMs, the efficiency is in the order of *p*-PtNT > *m*-PtNT > *m*-PmPNT. Lower efficiency for a device based on DPTNT might be attributed to its lower T_g and poor film-forming ability.

Fig. 5 shows EL characteristics of Group B compounds. As revealed in Fig. 5(a), the maximum current efficiencies of the devices based on CPPNN, *p*-PPtNN, *m*-PPtNN and *m*-PbPNN are 2.61, 2.18, 2.11 and 2.46 cd A^{-1} respectively. These are higher than the maximum current efficiencies of 1.60, 1.30 and 1.30 cd A^{-1} reported in similarly-structured devices using respectively Alq3 (as ETL), TPBI (as ETL) and BCP (as HBL)/Alq3 (as ETL).³¹⁻³⁶ Efficiencies of the devices based on CPPNN, *m*-PPtNN and *m*-PbPNN are especially high. The higher efficiencies might be attributed to their higher electron-transporting ability, as *p*-PPtNN has the lowest electron mobility among



Fig. 5 EL characteristics of devices based on the triphenylpyridine derivatives of Group B as ETL. Device structure: ITO/NPB [60 nm]/ ADN [30 nm]/a triphenylpyridine derivative [30 nm]/LiF [1 nm]/MgAg [100 nm 10 : 1]. (a): Current density (J)–voltage (V)–luminecence (L). (b): Current efficiency (η_L)–J–power efficiency (η_P). (c): EL spectra.

Group B. In particular, device based on CPPNN has the highest efficiency as CPPNN has the largest *IP* among Group B. In addition, it can be seen that the current efficiencies show only mild decreases as the current density increases. It can be seen from Fig. 5(b) that turn-on voltages (defined as the voltage required to deliver a luminance of 1 cd m⁻²) for the devices are in the range of 3.0 to 3.7 V only. These turn-on voltages are among the lowest values reported in similarly-structured blue emitting devices using other ETMs. Fig. 5(c) depicts EL spectra of the four devices using Group B compounds. EL spectra of the device respectively based on *m*-PPtNN and *m*-PbPNN show a peak at 452 nm, while those of the device based on CPPNN and

p-PPtNN respectively show peaks at 460 and 464 nm. λ_{FWHM} (full spectral widths at half maxima) of the four devices are respectively 87, 94, 67 and 71 nm. λ_{FWHM} of 67 nm for the device based on *m*-PbPNN is among the narrowest values³¹⁻³⁶ reported so far and the CIE coordinates of (0.15, 0.10) are the nearest to the coordinates of NTSC standards of (0.14, 0.08)³⁷ for blue emission. The better color purity is attributed to the good holeblocking properties of the triphenylpyridine derivatives which help to confine the emission zone within the ADN Layer. EL spectra of the device based on CPPNN are red-shifted to the sky blue region. This is possibly due to the 475 nm emission peak of CPPNN. λ_{FWHM} of the device based on *p*-PPtNN is obviously broader than those of the others. It may be attributed to the formation of exciplex in the ADN/p-PPtNN interface which can lead to red shift and EL peak broadening, because of the more deficient-electron molecular structure of p-PPtNN.

3. Conclusion

We have designed and synthesized two series of n-type materials based on triphenylpyridine derivatives, namely Group A: DPTNT, p-PPtNT, m-PPtNT and m-PmPNT; Group B: CPPNN, p-PPtNN, m-PPtNN and m-PbPNN. The triphenylpyridine derivatives with deep-blue emission show excellent thermal stabilities with high T_{g} and T_{m} . More importantly, these materials exhibit good electron-transporting abilities, large IPs and suitable EAs, which will be in favor of the electron transporting, hole blocking and electron injection in OLEDs. The deep-blue OLEDs were successfully fabricated by using the triphenylpyridine derivatives as the electron-transporting and holeblocking materials. The maximum current efficiency of these devices is above 2.10 cd A^{-1} , which is much higher than that of the devices with a similar device structure using the state-of-theart ETMs. The CIE coordinates of these devices are very close to the NTSC standard for blue emission. These results indicate that the triphenylpyridine derivatives are promising n-type ETMs, which could be used not only in different OLEDs, including fluorescent, phosphorescent, white emission devices, but also in organic thin-film transistors (OTFTs), etc. The relevant investigations are in progress in our laboratory.

4. Experimental section

4.1 General

Chemical structures of the two groups of triphenylpyridine derivatives are shown in Scheme 1. They were prepared using methods similar to those described in the literature.¹⁷ As all the compounds are made using a similar reaction sequence, a representative synthetic route for DPTNT is outlined in Scheme 2. Firstly, DPTNT I, *p*-PPtNT I, *m*-PPtNT I, *m*-PmPNT I, CPPNN I, *p*-PPtNN I, *m*-PPtNN I and *m*-PbPNN I (Scheme S1[†]) were respectively prepared by Claisen reactions between corresponding aromatic ketone and aromatic aldehyde. DPTNT, *p*-PPtNT, *m*-PPtNT, *m*-PPtNN, *m*-PPtNN, and *m*-PbPNN were then obtained by cyclocondensation of corresponding intermediate products with benzoylacetonitrile in the presence of ammonium acetate. These triphenylpyridine derivatives have been identified with ¹H NMR, ¹³C NMR and high-resolution mass spectrometry (HRMS).



Scheme 2 Synthetic routes for DPTNT.

Taking DPTNT as an example, benzaldehyde (1.06 g, 10 mmol) was first added to an alcohol solution of p-methyl acetophenone (2.00 g, 15 mmol) under stirring. A 10% NaOH solution (10 ml) was then dropped into the alcohol solution under rapid stirring. Stirring was continued for another 12 h. Solid powder was then collected, washed with H₂O, recrystallized with alcohol. White solid powder (DPTNT I) (1.92 g, 85% vield) were collected. The crystal (DPTNT I) (1.11 g, 5 mmol), benzoylacetonitrile (0.73 g, 10 mmol) and anhydrous ammonium acetate (0.5 g, 6.5 mmol) were added into a three-necked flask. Glacial acetic acid (50 ml) was then injected in under a nitrogen atmosphere. The mixture was refluxed for 24 h under stirring. The whole process was completed under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was filtered and crystallized with CH₂Cl₂/petroleum ether to obtain a white solid powder (DPTNT). p-PPtNT and m-PPtNT were obtained by recrystallization with 1,2-diclorobenzene. m-PmPNT was obtained via silicon gel column chromatography with CH_2Cl_2 /petroleum ether (3 : 1) as the eluent.

(*E*)-3-Phenyl-1-*p*-tolylprop-2-en-1-one (DPTNT I). ¹H NMR (400 MHz, CDCl₃, δ): 7.95 (d, J = 8.16 Hz, 2H), 7.83 (d, J = 15.72 Hz, 1H), 7.66–7.63 (m, 2H), 7.56 (d, J = 15.68 Hz, 1H), 7.43–7.41 (m, 3H), 7.31 (d, J = 7.96 Hz, 2H), 2.44 (s, 3H).

2,4-Diphenyl-6-*p*-tolylnicotinonitrile (DPTNT). ¹H NMR (400 MHz, CDCl₃, δ): 8.10 (d, J = 8.16 Hz, 2H), 8.05–8.02 (m, 2H), 7.79 (s, 1H), 7.69–7.67 (m, 2H), 7.58–7.54 (m, 6H), 7.33 (d, J = 8.04 Hz, 2H), 2.43 (s, 3H); ¹³C NMR (400 MHz, CDCl₃, δ): 162.5, 159.3, 155.5, 141.1, 138.3, 137.1, 134.9, 130.2, 130.0, 129.9, 129.5, 129.1, 128.8, 128.6, 127.6, 118.4, 118.0, 104.1, 21.6. HRMS (EI, *m/z*): [M⁺] calcd for C₂₅H₁₈N₂: 346.1470; found 346.1437 (Calcd. *m/z* 346.1470).

(2*E*,2'*E*)-3,3'-(1,4-Phenylene)bis(1-*p*-tolylprop-2-en-1-one) (*p*-PPtNT I). ¹H NMR (400 MHz, CDCl₃, δ): 7.96 (d, *J* = 8.12 Hz, 4H), 7.82 (d, *J* = 15.68 Hz, 2H), 7.69 (s, 4H), 7.60 (d, *J* = 15.68 Hz, 2H), 7.33 (d, *J* = 7.96 Hz, 4H), 2.45 (s, 6H).

4,4'-(1,4-Phenylene)bis(2-phenyl-6-*p***-tolylnicotinonitrile)** (*p*-**PPtNT).** ¹H NMR (400 MHz, CDCl₃, δ): 8.14 (d, J = 8.16 Hz, 4H), 8.08–8.05 (m, 4H), 7.90 (s, 2H), 7.88 (s, 4H), 7.58–7.56

(m, 6H), 7.35 (d, J = 8.08 Hz, 4H), 2.44 (s, 6H); ¹³C NMR (400 MHz, CDCl₃, δ): 162.6, 159.6, 154.4, 141.3, 138.4, 138.2, 134.7, 130.3, 130.0, 129.6, 128.7, 127.7, 118.4, 118.0, 103.9, 21.6. HRMS (EI, m/z): [M⁺] calcd for C₄₄H₃₀N₄: 614.2470; found: 614.2466.

(2*E*,2'*E*)-3,3'-(1,3-Phenylene)bis(1-*p*-tolylprop-2-en-1-one) (*m*-PPtNT I). ¹H NMR (400 MHz, CDCl₃, δ): 7.97 (d, J = 8.16 Hz, 4H), 7.87 (s, 1H), 7.84 (d, J = 15.68 Hz, 2H), 7.69–7.67 (m, 2H), 7.60 (d, J = 15.72 Hz, 2H), 7.50–7.48 (m, 1H), 7.33 (d, J = 8.00 Hz, 4H), 2.45 (s, 6H).

4,4'-(1,3-Phenylene)bis(2-phenyl-6-*p***-tolylnicotinonitrile)** (*m*-**PPtNT).** ¹H NMR (400 MHz, CDCl₃, δ): 8.13 (d, J = 8.16 Hz, 4H), 8.07–8.05 (m, 4H), 8.01 (s, 1H), 7.95 (s, 2H), 7.90–7.87 (m, 2H), 7.79–7.77 (m, 1H), 7.59–7.55 (m, 6H), 7.33 (d, J = 8.08 Hz, 4H), 2.43 (s, 6H); ¹³C NMR (400 MHz, CDCl₃, δ): 162.6, 159.6, 154.4, 141.3, 138.2, 137.7, 134.7, 130.3, 130.2, 129.9, 129.6, 129.4, 128.7, 127.7, 118.5, 118.1, 103.9, 21.6. HRMS (EI, *m/z*): [M⁺] calcd for C₄₄H₃₀N₄: 614.2470; found: 614.0865.

(2*E*,2'*E*)-3,3'-(1,3-Phenylene)bis(1-(4-methoxyphenyl)prop-2-en-1-one) (*m*-PmPNT I). ¹H NMR (400 MHz, CDCl₃, δ): 8.07 (d, J = 8.80 Hz, 4H), 7.87 (s, 1H), 7.84 (d, J = 15.68 Hz, 2H), 7.68– 7.66 (m, 2H), 7.61 (d, J = 15.68 Hz, 2H), 7.49–7.46 (m, 1H), 7.01 (d, J = 8.76, 4H), 3.90 (s, 6H).

4,4'-(1,3-Phenylene)bis(6-(4-methoxyphenyl)-2-phenylnicotinonitrile) (*m*-PmPNT). ¹H NMR (400 MHz, CDCl₃, δ): 8.21 (d, *J* = 8.72 Hz, 4H), 8.07–8.04 (m, 4H), 8.01 (s, 1H), 7.91 (s, 2H), 7.89–7.87 (m, 2H), 7.79–7.77 (m, 1H), 7.59–7.54 (m, 6H), 7.04 (d, *J* = 8.72 Hz, 4H), 3.88 (s, 6H); ¹³C NMR (400 MHz, CDCl₃, δ): 162.5, 162.1, 159.2, 154.3, 138.2, 137.7, 130.3, 130.1, 129.9, 129.8, 129.5, 129.4, 128.7, 118.3, 118.0, 114.6, 103.3, 55.6. HRMS (EI, *m/z*): [M⁺] calcd for C₄₄H₃₀N₄O₂: 646.2369; found: 646.2191.

(*E*)-4-(3-Oxo-3-phenylprop-1-enyl)benzonitrile (CPPNN I). ¹H NMR (400 MHz, CDCl₃, δ): 8.03–8.02 (m, 2H), 7.80–7.76 (m, 1H), 7.75–7.70 (m, 4H), 7.62–7.58 (m, 2H), 7.55–7.51 (m, 2H).

4-(4-Cyanophenyl)-2,6-diphenylnicotinonitrile (CPPNN). ¹H NMR (400 MHz, CDCl₃, δ): 8.19–8.17 (m, 2H), 8.05–8.00 (m, 2H), 7.88–7.86 (m, 2H), 7.82–7.78 (m, 3H), 7.76–7.52 (m, 6H); ¹³C NMR (400 MHz, CDCl₃, δ): 162.7, 159.8, 153.5, 141.3, 137.7, 137.2, 132.9, 131.1, 130.5, 129.7, 129.5, 129.2, 128.8, 127.7, 118.3, 118.2, 117.3, 114.0, 104.0. HRMS (EI, *m/z*): [M⁺] calcd for C₂₅H₁₅N₃: 357.1266; found: 357.1236.

(2*E*,2'*E*)-1,1'-(1,4-Phenylene)bis(3-*p*-tolylprop-2-en-1-one) (*p*-PPtNN I). ¹H NMR (400 MHz, CDCl₃, δ): 8.11 (s, 4H), 7.84 (d, *J* = 15.68 Hz, 2H), 7.57 (d, *J* = 8.08 Hz, 4H), 7.51 (d, *J* = 15.72 Hz, 2H), 7.26 (d, *J* = 8.48 Hz, 4H), 2.41 (s, 6H); ¹³C NMR (400 MHz, CDCl₃, δ):190.3, 146.0, 141.6, 141.5, 132.0, 129.9, 128.7, 121.0, 21.7.

6,6'-(1,4-Phenylene)bis(2-phenyl-4*p***-tolylnicotinonitrile)** (*p***-PtNN).** ¹H NMR (400 MHz, CDCl₃, δ): 8.32 (s, 4H), 8.06–8.04 (m, 4H), 7.87 (s, 2H), 7.62 (d, J = 8.08 Hz), 7.59–7.51 (m, 6H), 7.40 (d, J = 7.88 Hz, 4H), 2.47 (s, 6H); HRMS (EI, *m/z*): [M⁺] calcd for C₄₄H₃₀N₄: 614.2470; found: 614.2466.

(2*E*,2'*E*)-1,1'-(1,3-Phenylene)bis(3-*p*-tolylprop-2-en-1-one) (*m*-PPtNN I). ¹H NMR (400 MHz, CDCl₃, δ): 8.63 (s, 1H), 8.23–8.21 (m, 2H), 7.87–7.83 (m, 2H), 7.67–7.63 (m, 1H), 7.59–7.52 (m, 6H), 7.26–7.23 (m, 4H), 2.41 (s, 6H).

6,6'-(1,3-Phenylene)bis(2-phenyl-4-*p***-tolylnicotinonitrile)** (*m*-**PPtNN).** ¹H NMR (400 MHz, CDCl₃, δ): 8.90 (s, 1H), 8.31–8.29 (m, 2H), 8.07–8.04 (m, 4H), 7.88 (s, 2H), 7.69–7.65 (m, 1H), 7.61 (d, *J* = 8.08, 4H), 7.57–7.54 (m, 6H), 7.39 (d, *J* = 7.92 Hz, 4H), 2.46 (s, 6H); ¹³C NMR (400 MHz, CDCl₃, δ): 162.6, 158.7, 155.9, 140.5, 138.7, 138.1, 133.9, 130.3, 129.9, 129.8, 129.7, 129.6, 128.8, 128.7, 126.7, 118.9, 117.9, 104.9, 21.6. HRMS (EI, *m/z*): [M⁺] calcd for C₄₄H₃₀N₄: 614.2470; found: 614.2455.

(2*E*,2'*E*)-1,1'-(1,3-Phenylene)bis(3-(4-*tert*-butylphenyl)prop-2-en-1-one) (*m*-PbPNN I). ¹H NMR (400 MHz, CDCl₃, δ): 8.62 (s, 1H), 8.23–8.21 (m, 2H), 7.88 (d, *J* = 15.68 Hz, 2H), 7.66 (m, 1H), 7.63 (d, *J* = 8.36 Hz, 4H), 7.56 (d, *J* = 15.68 Hz, 2H), 7.47 (d, *J* = 8.40 Hz, 4H), 1.35 (s, 18H).

6,6'-(1,3-Phenylene)bis(4-(4*-tert*-butylphenyl)-2-phenylnicotinonitrile) (*m*-PbPNN). ¹H NMR (400 MHz, CDCl₃, δ): 8.88 (s, 1H), 8.31–8.29 (m, 2H), 8.07–8.05 (m, 4H), 7.89 (s, 2H), 7.69–7.55 (m, 15H), 1.39 (s, 18H); ¹³C NMR (400 MHz, CDCl₃, δ): 162.6, 158.6, 155.7, 153.5, 138.7, 138.1, 133.8, 130.2, 129.8, 129.6, 126.7, 126.2, 119.0, 117.9, 104.7, 35.0, 31.4. HRMS (EI, *m/z*): [M⁺] calcd. for C₅₀H₄₂N₄: 698.3409; found: 698.2701.

4.2 Thermal and spectral measurements

Thermal properties were characterized with TGA measurement at a ramping rate of 20 °C min⁻¹ and DSC measurement at a ramping rate of 10 °C min⁻¹ under nitrogen. Their *IP* were determined by using ultraviolet photoelectron spectroscopy (UPS). *EA* of individual compound was estimated by subtracting its optical transfer gap, as determined from UV-visible optical absorption spectroscopy, from the corresponding *IP*. The triplet energy (*E*_T) levels were estimated from the initial peak position of corresponding phosphorescent spectra.

4.3 Electron mobility measurements

Bilayer devices with the triphenylpyridine derivatives as the electron-transporting layers (ETLs) and NPB as the hole-transporting layer (HTL) were fabricated. The OLEDs have a configuration of ITO/NPB [60nm]/one of these triphenylpyridine derivatives [60nm]/MgAg [100nm, 10:1]. Using a pulse generator as an electrical switch in a high-current driver circuit, voltage pulses of 3-12V with a rise time less than 20 ns was obtained. The OLEDs were driven by the voltage pulses with duration of 2–25 µs. The luminance response from the device was detected by a silicon photo-diode attached to a high-speed receiver. The resulting transient photocurrent was analyzed with a storage oscilloscope (HP 54810A). For the interpretation of the luminance delay time, a voltage supply source was employed to give a trigger signal to start the collection of photocurrent. The transient responses of EL of all the devices were measured by averaging the data taken from 100 consecutive signals averaging.

4.4 OLED fabrication and measurements

The EL devices were fabricated on ITO coated glass substrates with a sheet resistance of 30 Ω \Box^{-1} . They were cleaned with Decon 90, rinsed in de-ionized water, dried in an oven and finally exposed to UV-ozone for about 25 min. The ITO substrates were then transferred into a deposition chamber with a base pressure of 5×10^{-7} mbar. Then organic layers were deposited at a rate of 0.1–0.2 nm s $^{-1}$ by conventional vapor vacuum deposition in 1 imes10⁻⁶ mbar. Then MgAg alloy was prepared by co-evaporation of Mg and Ag at a volume ratio of 10:1 after LiF of 1 nm was deposited. The EL characteristics are tested and analyzed in air. The current density-voltage-luminance characteristics were measured using a computer-controlled Keithley 2400 Sourcemeter. The EL spectra and CIE color coordinates were measured using Spectrascan PR650 photometer.

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