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Phenanthroimidazole-derivative semiconductors as functional layer in high performance OLEDs[†]

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Four phenanthroimidazole derivatives (**a**: 1,2-diphenyl-1*H*-phenanthro[9,10-*d*]imidazole; **b**: 2-phenyl-1-*p*-tolyl-1*H*-phenanthro[9,10-*d*]imidazole; **c**: 1-phenyl-2-*p*-tolyl-1*H*-phenanthro-[9,10-*d*]imidazole; **d**: 1,2-di-*p*-tolyl-1*H*-phenanthro[9,10-*d*]imidazole) were synthesized and their single crystal structures, photophysical, electrochemical and mobility properties were carefully studied. Taking advantage of the thermal stability and the hole transporting (HT) ability, the highly efficient Alq₃-based organic light-emitting diodes (OLEDs) have been achieved by employing the compounds **a**-**d** as a functional layer between NPB (4,4-bis(*N*-(1-naphthyl)-*N*phenylamino)biphenyl) and Alq₃ (tris(8-hydroxyquinoline)aluminium) layers. For the device of [ITO/NPB/**d**/Alq₃/LiF/Al], a maximum luminous efficiency (LE) of 8.1 cd A⁻¹ was obtained with a maximum brightness of 65 130 cd m⁻², which exhibited much higher efficiency compared to the device with structure of [ITO/NPB/Alq₃/LiF/Al]. The results demonstrated not only an alternative idea to design novel HT materials, but also a convenient way to improve the performance of the NPB/Alq₃-based devices by introduction of a suitable organic buffer layer.

Introduction

Since the observation of highly efficient electroluminescence (EL) from a bilayer device composed of triphenylamine derivative and tris(8-hydroxyquinoline)aluminium (Alq₃),¹ NPB (4,4-bis(N-(1-naphthyl)-N-phenylamino)biphenyl) and Alq₃ gradually became the most widely used hole-transporting, electron-transporting as well as host emitting materials in organic light-emitting diodes (OLEDs) due to their own many advantages such as thermal and morphological stability, and easy synthesis and purification.^{2–3} However, the electron and hole mobilities in Alq₃ and NPB are at the level of 10^{-4} – 10^{-5} and 10^{-3} - 10^{-4} cm² V⁻¹ s⁻¹, respectively, in an electric field of 2×10^6 V cm⁻¹,^{4,5} which gives rise to an accumulation of excess holes at the NPB/Alg₃ boundary. Great efforts have been invested to improve and balance carrier injection into the emitting layer to achieve high-efficiency devices. Among them, insertion of an anodic buffer layer including organic⁶ and inorganic⁷ materials between indium-tin oxide (ITO) and the hole-transporting layer (HTL) as a hole injection layer (HIL) could control the hole injection and have resulted in enhanced

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luminous efficiency (LE) and device duration. Enhancement and optimization of charge injection and transport and carrier balance are very important issues in achieving efficient devices.⁸ In this paper, we investigate the significant enhancement of the EL performance by inserting an organic buffer layer composed of a series of phenanthroimidazole derivatives⁹ with the thickness of tens of nanometres between the NPB and Alq₃ layer. Devices with structure of [ITO/NPB/ buffer layer/Alq₃/LiF/Al] were fabricated, which presented high brighness (>60 000 cd m⁻²) and efficiency (>8 cd A⁻¹). In addition, the characteristics of single crystal, thermal, photophysical, electrochemical, EL and hole mobility properties will be reported.

Results and discussion

X-Ray structures and molecular packing properties

Four phenanthroimidazole derivatives (**a**: 1,2-diphenyl-1*H*-phenanthro[9,10-*d*]imidazole; **b**: 2-phenyl-1-*p*-tolyl-1*H*-phenanthro[9,10-*d*]imidazole; **c**: 1-phenyl-2-*p*-tolyl-1*H*-phenanthro[9,10-*d*]imidazole; **d**: 1,2-di-*p*-tolyl-1*H*-phenanthro[9,10-*d*]-imidazole) have been synthesized. The single crystals of compounds **b**-**d** were obtained during sublimation. The molecular structures of compounds **b**-**d** were determined by single crystal X-ray crystallography. Fig. 1 shows the Oak Ridge thermal ellipsoid plot (ORTEP) drawing of **b**-**d**. Fig. 2 illustrates the molecular packing features of compounds **b**, **c**

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Fig. 1 ORTEP drawing of b-d with 30% thermal ellipsoids.

and **d** in crystals. In the asymmetric units for compounds **b** and c each have two independent molecules. In crystal b, there are two orientations of intermolecular interactions. In one orientation, intermolecular C–H $\cdots\pi$ interactions (2.67 Å) exist between the aniline and the phenanthrene plane. In another orientation, intermolecular C–H··· π interactions (2.81 Å) between the aniline and the phenanthrene plane are observed. There are intermolecular C–H···N interactions (2.71 Å) between two orientations. In the crystal of c, there are also two orientations of intermolecular interactions with the same C–H \cdot ··N interaction distance of 2.74 Å between phenyl and N atom of five-membered ring. Two kinds of intermolecular $C-H \cdot \cdot \pi$ interactions have been observed: (i) between phenyl and benzyl plane (2.66 Å), and (ii) between phenyl and phenanthrene plane (2.63 Å) in two orientations. In solid \mathbf{d} , there are just intermolecular hydrogen bonding interactions between benzyl and benzyl (2.89 Å), and between phenanthrene and phenanthrene (2.89 Å). There is no interfacial $\pi \cdots \pi$ interaction in the packing structure of **b**-**d**.

Thermal analysis

The thermal properties of **a-d** were investigated by differential scanning calorimetry (DSC) and thermal gravimetric analyses (TGA) under a nitrogen atmosphere (Fig. 3). The melting points of **a-d** measured by DSC examinations were 206, 211, 199 and 194 °C, respectively. Compound **b** has the highest melting point among these compounds, which is probably due to the intermolecular C–H··· π interactions of two orientations that can induce more condensed molecular packing. The decomposition temperatures with a 5% weight loss (T_{ds}) for **a-d** are 343, 342, 337, 336 °C, respectively. The high T_m and T_{d5} values indicate that the compounds **a-d** are thermally stable and would be capable of enduring the vacuum thermal sublimation process, which might serve as an advantage when



Fig. 2 Stacking diagram showing intermolecular interactions in solid **b**, **c** and **d**.

these complexes are used in EL devices since the high $T_{\rm m}$ and $T_{\rm g}$ values could improve the lifetime of the devices.¹⁰ The $T_{\rm g}$ (glass transition temperature) values are 82, 74, 74 and 64 °C for **a**, **b**, **c** and **d** (Table 1), respectively.

Photophysical and electrochemical properties

Absorption and photoluminescence studies were performed on compounds **a**–**d** in chloroform (10^{-4} M) to investigate the relationship between methyl substituents and the physical properties (Fig. 4). For all the compounds, their absorption spectra do not show remarkable differences and have a maxima at 262 nm and a shoulder at around 311 nm suggesting the very similar optical energy gap. The photoluminescence spectra of compounds **a** and **b** have a same sharp emission peak at 384 nm accompanied by a shoulder around 370 nm, and a slight red shift of the emission bands for compounds **c** and **d** with the peak of 387 nm and the shoulder of 373 nm



Fig. 3 DSC (top) and TGA (bottom) curves of compounds $\mathbf{a}-\mathbf{d}$ at a heating rate of 10 °C min⁻¹.

Table 1 Thermal, electrochemical and photophysical data of a-d

	$T_{\rm m}/T_{\rm g}/T_{\rm d5}/^{\circ}{\rm C}$	$\lambda_{max,abs}/nm^a$	$\lambda_{\rm em}/{\rm nm}^a$	$E_{\rm ox}/{\rm V}$	HOMO/LUMO/eV ^b
a	206/82/343	262,311	384,370	0.84	-5.64/-2.29
b	211/74/342	262,311	384,370	0.82	-5.62/-2.27
c	199/74/337	262,311	387,373	0.80	-5.60/-2.27
d	194/64/336	263,311	387,374	0.78	-5.58/-2.24

^{*a*} In CHCl₃. ^{*b*} The HOMO and LUMO energies were determined from cyclic voltammetry and absorption data.



Fig. 4 UV-Vis absorption and PL spectra (normalized) in $CHCl_3$ (10⁻⁴ M) compounds **a-d**.

were observed. No major difference has been shown between the photophysical properties of all the compounds **a-d** indicating that the substitution of methyl has little effect on the photophysical properties of a-d. The electrochemical properties of compounds **a-d** were studied in solution through cvclic voltammetry (CV) measurements using ferrocene as the internal standard. Their cyclic voltammograms are shown in Fig. 5 and the respective electrochemical data are summarized in Table 1. All the compounds a-d displayed one reversible oxidation wave and no reduction wave was detected within the electrochemical window of dichloromethane. The introduction and the increased amount of methyl groups only lead a slight negative shift respect to oxidation potentials from compound a to d (0.84 V, 0.82 V, 0.80 V and 0.78 V, respectively). The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of compounds were calculated from the onset potentials for oxidation together with their absorption spectra. The HOMO energy levels varied from -5.64 eV for compound a to -5.62 eV, -5.60 eV, -5.58 eV for compound **b**, **c** and **d**, and the corresponding LUMO levels were -2.29 eV, -2.27 eV, -2.27 eV and -2.24 eV, respectively.

Electroluminescence and mobility properties

To investigate the EL properties of compounds a-d as a buffer layer, a series of devices (I, II, III and IV) with the device configuration of [ITO/NPB (10 nm)/buffer layer (30 nm)/Alq₃ (60 nm)/LiF (1 nm)/Al] have been fabricated, where NPB was the hole-transporting layer (HTL), Alq₃ was employed as the electron-transporting layer (ETL) and the emitting layer (EML). The compound **a-d** film was the buffer layer in device I, II III and IV, respectively. For comparison, the reference device (device V) with the structure of [ITO/NPB (40 nm)/Alq₃ (60 nm)/LiF/Al] and device VI with the thiner layer (10 nm) of compound d by maintaining the total thickness (40 nm) of HTL and buffer layer were fabricated also. Fig. 6 and 7 show the current density-brightness-voltage and the luminous efficiency (LE)-current density characteristics, respectively. The devices exhibited bright green emission (Fig. 8) from Alq₃, independent of the applied voltages in the range of 3 V to 16 V. At the same driven voltage, the current density and the EL intensity of devices I-IV with a buffer layer was much





Fig. 6 Current density-brightness-voltage characteristics of devices I, II, III, IV and V. Current density-voltage characteristics of VI.



Fig. 7 Luminous efficiency (LE)-current density characteristics of devices I-V.

lower than those of device V. However, the devices I-IV exhibited higher LE than that of device V. For instance, at an injection current density of 100 mA cm⁻², the LE of of device V without buffer layer is 3.1 cd A^{-1} , while device I–IV is 5.4, 4.1, 3.8, 6.4 cd A^{-1} , respectively. Furthermore, all the devices containing buffer layer showed very high peak brightness and color stability under different driving voltage. Among them, device IV based on compound **d** had the highest efficiency among all the devices, the peak LE of 8.1 cd A^{-1} was obtained at the peak brightness of 65 130 cd m^{-2} at 15 V. This is rather high EL efficiency under such high-level brightness for the OLED based on fluorescent materials, which has been significantly enhanced also compared to that of device V $(3.22 \text{ cd } A^{-1} \text{ at } 27390 \text{ cd } m^{-2} \text{ and } 10.5 \text{ V})$. Obviously, the presence of the buffer layer between the NPB and Alq₃ layers could increase the LE value. We believed that the improved efficiency of the devices I-IV is due to the decrease of the amount of holes through the buffer layer, which results in balancing the electrons and holes in the emitting layer and thus eliminating the nonproductive hole current. From the electrochemical data of the materials used in the devices listed in Table 1, the HOMO energy level of compounds **a-d** is about -5.6 eV, which is in between that of NPB (-5.4 eV) and Alq₃ $(-6.0 \text{ eV})^{11}$ and could regulate the hole injection by acted as a ladder between the energy levels of NPB and Alq₃.^{6a,b,12}

Therefore, the decreased amount of holes should be attributed to the relatively low HT ability of compounds **a**–**d**, which is supported by the current density–voltage characteristic of device IV and VI with different thickness of buffer layer based on compound **d** (Fig. 6).¹³ The current density of device IV with thicker compound **d** layer was much lower than that of device V with the traditional device structure. For the device VI with thinner compound **d** layer, it showed a higher current density than that of device V. The dependence of the current density of device on the thickness of buffer layer indicates compound **d** and the series of phenanthroimidazole derivatives can prevent excessive holes to enter the EML when the thickness of functional layer is as thick as tens nanometres. The higher efficiency was realized by improving the balance of the hole and electron.

Furthermore, the hole mobility of compound **d** was measured using the conventional time of flight (TOF) technique based on the device configuration of [ITO/**d** (1.36 μ m)/Al].¹⁴ Fig. 9 shows typical TOF transients of holes for complex **d** under an applied field, and the transient photocurrent signals were dispersive, suggesting the presence of charge carrier traps. The hole mobility of compound **d** was determined to be 3.4 × 10⁻⁴ cm² V⁻¹ s⁻¹, while that of the commonly used HT material NPB is 7.4 × 10⁻⁴ cm² V⁻¹ s⁻¹ based on the same measurement condition. Clearly, the hole-mobility alignment of compound **d** can decrease the amount of holes transported into the emitting layer effectively due to its relatively low hole mobility.

The compounds **a**–**d** with almost alike molecular structures exhibit similar thermal, electrochemical and photophysical properties. However, the devices I–IV displayed different turn on voltage, highest brightness and maxima LE (Table 2). We tentatively attribute the different EL property to the difference of molecular packing and nanostructures of **a**–**d** in thin film systems. The charge transport of organic semiconductors is strongly molecular packing and morphology dependent. It has been demonstrated that organic molecules with similar molecular structures exhibited remarkably different mobility.¹⁵ On the other hand, in EL devices the carrier mobility and balance is often dependent on the interfacial characteristics between the buffer layer and NPB or Alq₃ layer, which have effect on the EL performance. At this stage, we can not provide rational explanation for this phenomenon.



Fig. 8 The EL spectra of devices I-VI at applied voltages of 9 V.



Fig. 9 TOF transient of complex **d** for hole at room temperature $(E = 4.4 \times 10^5 \text{ V cm}^{-1} \text{ and } T_t = 0.9 \text{ }\mu\text{s})$. Insert: log of the photocurrent *vs.* the log of time in a time-of-flight measurement.

 Table 2
 Performance of OLEDs^a

Device	$V_{\rm on} \left({\rm V} \right)^b$	$L (cd m^{-2})$	$\eta_{\rm c} \; ({\rm cd} \; {\rm A}^{-1})$	CIE(x,y)@9 V
I	5.0	35970	6.10	(0.33,0.55)
II	4.9	24220	4.07	(0.32, 0.55)
III	4.1	33680	4.16	(0.33, 0.55)
IV	3.8	65130	8.03	(0.35,0.56)
V	2.7	37360	3.22	(0.32, 0.52)
VI	2.7	38910	4.17	(0.32,0.52)

^{*a*} The brightness (*L*) and current efficiency (η_c) are the maximum values of the devices. ^{*b*} V_{on} is defined as the voltage required for 1 cd m⁻¹².

Conclusions

Four phenanthroimidazole derivatives (a, b, c and d) have been synthesized and the detailed studies of their single crystal structures, photophysical and electrochemical properties are presented. The high $T_{\rm m}$ and $T_{\rm d5}$ values indicate that these compounds are thermally stable and can be used to fabricate efficient EL devices. The highly efficient Alq3-based EL devices have been achieved by employing compound **a-d** as an organic buffer layer inserted between NPB and Alq₃ layers. A maximum LE of 8.1 cd A^{-1} was obtained with a maximum brightness of 65130 cd m⁻² at 15 V, which exhibited much higher efficiencies compared with the device of [ITO/NPB/ Alq₃/LiF/Al] without **a-d**. This improvement is due to the relatively weak HT ability of the phenanthroimidazole derivatives, which can depress excessive holes to transport into the EML, thus improve the balance of the hole and electron and realize the higher efficiency. The results of this study not only demonstrated an alternative idea to design novel HT materials, but also provided a convenient way to improve the performance of the NPB/Alq₃-based devices by inserting a suitable organic buffer layer.

Experimental

General information

All reactants and solvents, unless otherwise stated, were purchased from commercial sources and used as received. ¹H NMR spectra were measured on a Bruker AVANCE 500 MHz

spectrometer with tetramethylsilane as the internal standard. Mass spectra were recorded on a Shimadzu AXIMA-CFR MALDITOF mass spectrometer. Elemental analyses were performed on a flash EA 1112 spectrometer. Differential Scanning Calorimetric (DSC) measurements were performed on a NETZSCH DSC204 instrument. Thermogravimetric analyses (TGA) were performed on a TAQ500 thermogravimeter. UV-vis absorption spectra were recorded using a PE UV-vis lambdazo spectrometer. The emission spectra were recorded using a Shimadzu RF-5301 PC spectrometer. The IR spectra were obtained on a FT-IR Vertex 80 V spectrometer. Cyclic voltammetry was performed on a BAS 100 W instrument with a scan rate of 100 mV s^{-1} . A three-electrode configuration was used for the measurement: a platinum electrode as the working electrode, a platinum wire as the counter electrode, and an Ag/Ag^+ electrode as the reference electrode. A 0.1 M solution of tetrabutylammonium perchlorate (TBAPF₆) in CH₂Cl₂ was used as the supporting electrolyte. Prior to device fabrication, all the compounds were purified by gradient sublimation.

Preparation of phenanthroimidazole derivatives

The synthetic route of phenanthroimidazole derivatives is shown in Scheme 1. The preparation of 1,2-diphenyl-1*H*phenanthro[9,10-*d*]imidazole (compound **a**) is employed as an example to describe the synthesis procedure. A mixture of phenanthrene-9,10-dione (2.0 g, 9.6 mmol), benzaldehyde (1.02 g, 9.6 mmol), aniline (4.46 g, 48 mmol), ammonium acetate (2.96 g, 38.4 mmol) and glacial acetic acid (60 mL) was heated at 123 °C for 3 h under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was poured into distilled water with stirring. The separated solid was filtered off, washed with water and dried to give the expected product in good yields. The yields and characterization data are given below.

1,2-Diphenyl-1*H***-phenanthro**[**9,10-***d***]imidazole (a).** Yield: 65%. MS: m/z 370.5 (M⁺). ¹H NMR (500 MHz, d_6 -DMSO) δ (ppm): 7.09 (d, J = 7.5 Hz, 1H), 7.33–7.40 (m, 4H), 7.55–7.60 (m, 3H), 7.68–7.72 (m, 6H), 7.78 (t, J = 7 Hz, 1H), 8.70 (d, J = 7 Hz, 1H), 8.88 (d, J = 8.5 Hz, 1H), 8.93 (d, J =8.5 Hz, 1H). Anal. calcd (%) for C₂₇H₁₈N₂: C, 87.54; H, 4.90; N, 7.56. Found: C, 87.43; H, 4.95; N, 7.62. IR (cm⁻¹): 428 (w), 517 (w), 534 (w), 613 (w), 667 (w), 700 (s), 710 (m), 720 (s), 753 (s), 776 (s), 806 (w), 1035 (w), 1070 (w), 1106 (w), 1121 (w),



1147 (w), 1167 (w), 1233 (w), 1344 (w), 1383 (s), 1452 (s), 1496 (s), 1523 (w), 1596 (w), 3056 (m).

2-Phenyl-1*p***-tolyl-1***H***-phenanthro** [9,10-*d*]imidazole (b). Yield: 55%. MS: m/z 384.6 (M⁺). ¹H NMR (500 MHz, d_6 -DMSO) δ (ppm): 2.35 (s, 3H), 7.14 (d, J = 8.5 Hz, 1H), 7.34–7.37 (m, 4H), 7.47 (d, J = 8 Hz, 2H), 7.538–7.599 (m, 5H), 7.68 (t, J = 7.5 Hz, 1H), 7.77 (t, J = 7.5 Hz, 1H), 8.68 (d, J = 8 Hz, 1H), 8.87 (d, J = 8.5 Hz, 1H), 8.92 (d, J = 8.5 Hz, 1H). Anal. calcd (%) for C₂₈H₂₀N₂: C, 87.47; H, 5.24; N, 7.29. Found: C, 87.30; H, 5.33; N, 7.37. IR (cm⁻¹): 428 (w), 520 (w), 533 (w), 615 (w), 662 (m), 697 (s), 725 (s), 755 (s), 775 (m), 802 (w), 833 (m), 917 (w), 954 (w), 977 (w), 1020 (w), 1075 (w), 1102 (w), 1145 (m), 1324 (m), 1345 (m), 1384 (s), 1450 (s), 1470 (s), 1512 (s), 1573 (m), 1611 (m), 1907 (w), 2954 (w), 3063 (w).

1-Phenyl-2-*p*-tolyl-1*H*-phenanthro [9,10-*d*] imidazole (c). Yield: 50%. MS: *m*/*z* 384.6 (M⁺). ¹H NMR (500 MHz, *d*₆-DMSO) δ (ppm): 2.29 (s, 3H), 7.07 (d, *J* = 8 Hz, 1H), 7.15 (d, *J* = 8 Hz, 2H), 7.33 (t, *J* = 8 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.55 (t, *J* = 7 Hz, 1H), 7.67–7.72 (m, 6H), 7.77 (t, *J* = 7.5 Hz, 1H), 8.68 (d, *J* = 8 Hz, 1H), 8.87 (d, *J* = 8.5 Hz, 1H), 8.92 (d, *J* = 8.5 Hz, 1H). Anal. calcd (%) for C₂₈H₂₀N₂: C, 87.47; H, 5.24; N, 7.29. Found: C, 87.38; H, 5.32; N, 7.30. IR (cm⁻¹): 428 (w), 511 (w), 520 (w), 534 (w), 614 (w), 659 (w), 671 (w), 698 (s), 709 (m), 726 (s), 755 (s), 771 (w), 822 (m), 921 (w), 948 (w), 1036 (w), 1143 (w), 1188 (w), 1237 (w), 1284 (w), 1235 (w), 1379 (s), 1426 (w), 1450 (s), 1470 (s), 1495 (s), 1513 (w), 1577 (w), 1594 (w), 1610 (w), 3059 (m).

1,2-Di-*p*-tolyl-1*H*-phenanthro [9,10-*d*]imidazole (d). Yield: 60%. MS: m/z 398.6 (M⁺). ¹H NMR (500 MHz, d_6 -DMSO) δ (ppm): 2.30 (s, 3H), 2.35 (s, 3H), 7.127–7.173 (m, 3H), 7.35 (t, J = 7.5 Hz, 1H), 7.47 (d, J = 8 Hz, 4H), 7.55 (d, J = 8.5Hz, 3H), 7.68 (t, J = 7.5 Hz, 1H), 7.76 (t, J = 8 Hz, 1H), 8.67 (d, J = 8 Hz, 1H), 8.87 (d, J = 8.5 Hz, 1H), 8.92 (d, J = 8 Hz, 1H). Anal. calcd (%) for C₂₉H₂₂N₂: C, 87.41; H, 5.56; N, 7.03. Found: C, 87.23; H, 5.68; N, 7.09. IR (cm⁻¹): 430 (w), 506 (w), 529 (w), 671 (m), 724 (s), 755 (s), 773 (w), 816 (m), 837 (m), 855 (w), 870 (w), 950 (w), 975 (w), 992 (w), 1017 (w), 1035 (w), 1106 (w), 1142 (w), 1184 (w), 1235 (w), 1280 (w), 1327 (w), 1379 (s), 1428 (m), 1450 (s), 1470 (s), 1513 (s), 1578 (w), 1610 (w), 2918 (m), 3033 (m).

Single crystal X-ray diffraction

The single crystals suitable for X-ray structural analysis were obtained by vacuum sublimation. Diffraction data were collected on a Rigaku R-Axis Rapid diffractometer (Mo-K α radiation, graphite monochromator) in the ψ rotation scan mode. The structure determination was performed by direct methods using SHELXTL 5.01v and refinements with full-matrix least squares on F^2 .

Crystal data for **b**: CCDC 806932; $C_{28}H_{20}N_2$; FW = 384.5, triclinic, *P*-1, *a* = 9.776(2) Å, *b* = 12.364(3) Å, *c* = 18.480(4) Å, $\alpha = 73.75(3)^\circ$, $\beta = 80.53(3)^\circ$, $\gamma = 76.89(3)^\circ$, $V = 2076.3(7) Å^3$, Z = 4, $D_c = 1.230$ g cm⁻³. The refinement converged to $R_1 =$ 0.0465, w $R_2 = 0.1234$ ($I > 2\sigma(I)$), GOF = 1.05.

Crystal data for **c**: CCDC 806933; $C_{28}H_{20}N_2$; FW = 384.5, orthorhombic, $P_{21}2_{12}$, a = 10.527(2) Å, b = 18.843(4) Å,

 $c = 20.461(4) \text{ Å}, \alpha = 90^{\circ}, \beta = 90^{\circ}, \gamma = 90^{\circ}, V = 4058.6(14) \text{ Å}^3,$ $Z = 8, D_c = 1.258 \text{ g cm}^{-3}$. The refinement converged to $R_1 = 0.0732, \text{ w}R_2 = 0.1100 (I > 2\sigma(I)), \text{ GOF} = 0.984.$

Crystal data for **d**: CCDC 806934; C₂₉H₂₂N₂; FW = 398.5, monoclinic, $P2_1/c$, a = 13.726(3) Å, b = 8.4643(17) Å, c = 19.367(4) Å, $\alpha = 90^{\circ}$, $\beta = 109.14(3)^{\circ}$, $\gamma = 90^{\circ}$, V = 2125.6(7) Å³, Z = 4, $D_c = 1.245$ g cm⁻³. The refinement converged to $R_1 = 0.0740$, w $R_2 = 0.1596$ ($I > 2\sigma(I)$), GOF = 1.025.

Device fabrication and measurements

ITO coated glass was used as the substrate. It was cleaned by sonication successively in a detergent solution, acetone, methanol, and deionized water before use. The devices were prepared in vacuum at a pressure of 5×10^{-6} torr. Organic layers were deposited onto the substrate at a rate of 0.1 nm s⁻¹. After the organic film deposition, LiF and aluminum were thermally evaporated onto the surface of organic layer. The thicknesses of the organic materials and the cathode layers were controlled using a quartz crystal thickness monitor. The electrical characteristics of the devices were measured with a Keithley 2400 sourcemeter. The EL spectra and luminance of the devices were obtained on a PR650 spectrometer. All measurements of the devices were carried out in ambient atmosphere without further encapsulations.

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References

- (a) C. W. Tang and S. A. Vanslyke, *Appl. Phys. Lett.*, 1987, **51**, 913; (b) C. W. Tang, S. A. Vanskyke and C. H. Chen, *J. Appl. Phys.*, 1989, **65**, 3610.
- (a) M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson and S. R. Forrest, *Nature*, 1998, **395**, 151;
 (b) X. H. Zhang, B. J. Chen, X. Q. Lin, O. Y. Wong, C. S. Lee, H. L. Kwong, S. T. Lee and S. K. Wu, *Chem. Mater.*, 2001, **13**, 1565; (c) K. Q. Ye, J. Wang, H. Sun, Y. Liu, Z. C. Mu, F. Li, S. M. Jiang, J. Y. Zhang, H. X. Zhang, Y. Wang and C.-M. Che, *J. Phys. Chem. B*, 2005, **109**, 8008; (d) H. Bi, K. Q. Ye, Y. F. Zhao, Y. Yang, Y. Liu and Y. Wang, *Org. Electron.*, 2010, **11**, 1180.
- 3 L. S. Hung and C. H. Chen, Mater. Sci. Eng., R, 2002, 39, 143
- 4 (a) G. G. Malliaras, Y. Shen, D. H. Dunlap, H. Murata and Z. H. Kafafi, *Appl. Phys. Lett.*, 2001, **79**, 2582; (b) S. C. Tse, H. H. Fong and S. K. So, *J. Appl. Phys.*, 2003, **94**, 2033; (c) S. C. Tse, S. K. So, M. Y. Yeung, C. F. Lo, S. W. Wen and C. H. Chen, *Jpn. J. Appl. Phys.*, 2006, **45**, 555.
- 5 (a) S. C. Tse, K. C. Kwok and S. K. So, *Appl. Phys. Lett.*, 2006, 89, 262102; (b) K. K. Tsung and S. K. So, *Appl. Phys. Lett.*, 2008, 92, 103315.
- (a) Y. Shirota, Y. Kuwabara, H. Inada, T. Wakimoto, H. Nakada,
 Y. Yonemoto, S. Kawami and K. Imai, *Appl. Phys. Lett.*, 1994, 65, 807; (b) S. A. VanSlyke, C. H. Chen and C. W. Tang, *Appl. Phys. Lett.*, 1996, 69, 2160; (c) S. A. Carter, M. Angelopoulos, S. Karg,
 P. J. Brock and J. C. Scott, *Appl. Phys. Lett.*, 1997, 70, 2067.
- 7 (a) Z. B. Deng, X. M. Ding, S. T. Lee and W. A. Gambling, *Appl. Phys. Lett.*, 1999, **74**, 2227; (b) H. J. Jiang, Y. Zhou, B. S. Ooi, Y. W. Chen, T. Wee, Y. L. Lam, J. S. Huang and S. Y. Liu, *Thin Solid Films*, 2000, **363**, 25; (c) C. F. Qiu, H. Y. Chen, Z. L. Xie, M. Wong and H. S. Kwok, *Appl. Phys. Lett.*, 2002, **80**, 3485; (d) Y. Kurosaka, N. Tada, Y. Ohmori and K. Yoshino, *Synth. Met.*, 1999, **102**, 1101; (e) I. M. Chan, T. Y. Hsu and E. C. Hong,

Appl. Phys. Lett., 2002, **81**, 1899; (f) W. P. Hu, M. Matsumura, K. Furukawa and K. Torimitsu, J. Phys. Chem. B, 2004, **108**, 13116.

- 8 (a) J. Kwon, T. H. Kwon, H. S. Cho, M. K. Kim, I. S. Shin, D. Y. Shin, S. J. Park and J. I. Hong, *New J. Chem.*, 2008, **32**, 1368–1372; (b) L. Aubouy, N. Huby, L. Hirsch, A. van der Lee and P. Gerbier, *New J. Chem.*, 2009, **33**, 1290–1300.
- 9 I. Yoshikatsu and M. Teruo, J. Org. Chem., 1979, 44, 41.
- 10 (a) S. Tokito, H. Tanaka, K. Noda, A. Okada and Y. Taga, *Appl. Phys. Lett.*, 1997, **70**, 1929; (b) Z. K. Chen, H. Meng, Y. H. Lai and W. Huang, *Macromolecules*, 1999, **32**, 4351; (c) T.-R. Chen,

R.-H. Chien, M.-S. Jan, A. Yeh and J.-D. Chien, *J. Organomet. Chem.*, 2006, **691**, 799.

- (a) T. Tsuzuki and S. Tokito, Adv. Mater., 2007, 19, 276;
 (b) C. Adachi, M. E. Thompson and S. R. Forrest, IEEE J. Sel. Top. Quantum Electron., 2002, 8, 372.
- 12 C. Adachi, K. Nagai and N. Tamoto, Appl. Phys. Lett., 1995, 66, 2679.
- 13 L. X. Xiao, S.-J. Su, Y. Agata. H. Lan and J. Kido, Adv. Mater., 2009, 21, 1271.
- 14 H. H. Fong, K. C. Lun and S. K. So, Chem. Phys. Lett., 2002, 353, 407.
- 15 Z. X. Xu, H. F. Xiang, V. A. Roy, S. S. Y. Chui, Y. Wang, P. T. Lai and C. M. Che, *Appl. Phys. Lett.*, 2009, **95**, 123305.