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Strongly phosphorescent platinum(II) complexes supported by tetradentate benzazole-containing ligands[†]

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A series of strongly phosphorescent Pt(II) complexes (Pt1–Pt3) supported by rigid benzazole-containing tetradentate ligands (L1–L3) were designed and synthesized. The effect of heteroatoms (S, O and N) on the photophysical and electroluminescence properties of Pt(II) complexes was studied systematically. Complex Pt1 based on the benzothiazole-containing ligand exhibited a red-shift in UV-vis and photoluminescence spectra in comparison with Pt2 and Pt3 due to the low electro-negativity and high polarizability of the S atom. Organic light-emitting diodes (OLEDs) with various doping levels of these Pt(II) phosphors were fabricated. At low complex concentration, Pt1, Pt2 and Pt3 mainly showed high energy monomer emission. When the doping ratio was increased, low energy excimer emission was observed for both Pt1 and Pt2. On the contrary, Pt3 dominantly showed monomer emission even at a high doping level because the strong intermolecular interactions were greatly suppressed due to the presence of bulky alkyl chains as revealed by X-ray crystallographic analysis. OLEDs based on these complexes exhibited yellowish green to greenish yellow electro-phosphorescence with high efficiency. Notably, the device based on Pt3 at the doping level of 10 wt% achieved a maximum efficiency of 75.0 cd A⁻¹, 70.1 lm W⁻¹ and 21.4% with Commission Internationale de L'Eclairage (CIE) coordinates of (0.33, 0.61).

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Introduction

Organic light-emitting diodes (OLEDs) have attracted great attention due to their applications in energy efficient displays, solid state lighting, and various electronic devices and accessories. Phosphorescent Ir(m) and Pt(n) complexes have been widely studied to achieve high efficiency OLEDs since their electroluminescence can be generated from both singlet and triplet excited states, and thus they can harvest 100% of electrogenerated excitons.¹ During the last decade Ir(m) complexes have been the mainstream light emitters in OLEDs.² Recently platinum(n) complexes bearing rigid tetradentate ligands have emerged as an important class of phosphorescent materials because their rigid structure can reduce the probability of nonemissive decay from ligand-centered excited states (${}^{3}\pi-\pi^{*}$) and metal-to-ligand charge-transfer (MLCT) excited states through suppressing the vibration and rotation around metal ions, thus leading to high luminescence efficiency.³ Meanwhile the chelated Pt(n) complexes showed very high thermal stability. By employing rigid tetradentate Pt(n) complexes, Li *et al.* demonstrated efficient pure blue OLEDs with an external quantum efficiency (EQE) of 22.7% at 100 cd m⁻² and Commission Internationale de L'Eclairage (CIE) coordinates of (0.148, 0.079).⁴ By using structurally robust phosphorescent [Pt(O^NC^NN]] emitters, Che and coworkers achieved a high power efficiency of up to 126 lm W⁻¹ and an EQE over 20%.⁵

By now many platinum(π) complexes with symmetric/ asymmetric tetradentate ligands have been reported with their emission energy ranging from blue to red.^{3–6} Generally the Pt(π) ion adopts a square planar coordination geometry, which is favorable for the mononuclear Pt(π) complex to form a tight packing pattern *via* strong intermolecular interaction. The electroluminescence properties of a Pt(π) complex could be tuned significantly after aggregation of the planar molecules. For example, a tetradentate Pt(π) complex Pt₂O₂ was used as a single emissive material to fabricate efficient and stable excimerbased white OLEDs (WOLEDs).⁷ Our interest in this area is to develop robust phosphorescent Pt(π) complexes supported by benzazole-containing ligands. Benzazoles are benzothiazole/ benzoxazole/benzimidazole-based derivatives (Scheme 1), a novel



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Scheme 1 Molecular structures of benzazoles (left) and benzazolecontaining ligands L1–L3 (right).

class of N,O-chelate ligands, which could form sublimable luminescent materials as dopants in OLEDs.⁸ It was reported that hetero-atoms of benzazole ligands played an important role in tuning the luminescence properties of metal complexes.^{8a,b} So far benzazole-based Ir(III) and Pt(II) complexes have been rarely reported,⁹ where benzazole derivatives serve merely as bidentate [N^O] ligands. On the other hand, the bidentate benzazole ligands were labile and could be detached from the metal complex upon treatment with acid^{9c} and addition of other metal ions.^{9e} In this paper, we incorporated a benzazole motif into tetradentate ligands L1, L2 and L3 (Scheme 1) to enhance the stability of resultant Pt(II) complexes (**Pt1–Pt3**, Scheme 2), and further to study the effect of heteroatoms on photoluminescence/electroluminescence properties of this series of Pt(II) complexes systematically. OLEDs based on these Pt complexes exhibited excellent device performance. Particularly, **Pt3** achieved a maximum efficiency of 75.0 cd A^{-1} , 70.1 lm W⁻¹ and 21.4% with CIE coordinates of (0.33, 0.61).

Results and discussion

Preparation and characterization

Scheme 1 outlines the synthetic routes of tetradentate ligands L1–L3 and Pt complexes Pt1–Pt3. L1, L2 and L3 were synthesized by Suzuki coupling of 2-(3-(*tert*-butyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyridine with 2-(4-bromo-benzothiazol-2-yl)phenol,¹⁰ 2-(4-bromo-benzoxazol-2-yl)-phenol¹¹ and 2-[4-bromo-1-(2-ethylhexyl)-1*H*-benzoimidazol-2-yl]phenol, respectively. Initially ligand L3 was designed and synthesized without the 2-ethylhexyl group attached to the N atom. However the desired compound showed very poor solubility in common organic solvents, which renders it intractable to purification. The target Pt(π) complexes Pt1, Pt2 and Pt3 were synthesized *via* one-pot reaction of K₂PtCl₄



Scheme 2 The synthetic routes to Pt(II) complexes Pt1, Pt2 and Pt3.

and tetradentate ligands L1, L2 and L3, respectively. All platinum(II) complexes were purified by column chromatography over silica gel and then subjected to sublimation (the sublimation temperature: <330 °C at 1×10^{-4} Pa and the yield of sublimation: >90% for Pt1–Pt3) before they are subject to device fabrication. They were fully characterized by ¹H and ¹³C NMR, MALDI-TOF mass spectrometry, and elemental analysis.

The thermal stability of **Pt1**, **Pt2** and **Pt3** was determined by thermogravimetric analysis under N₂. These Pt(π) complexes exhibited excellent thermal stability with 5% weight-reduction temperatures ($\Delta T_{5\%}$) of 453 °C for **Pt1**, 420 °C for **Pt2**, and 407 °C for **Pt3**, which allows device fabrication by a vacuum deposition method.

The electrochemical properties of these complexes were examined by cyclic voltammetry. All these Pt(II) complexes showed an irreversible oxidation process, which is typical for tetradentate Pt(II) complexes.¹² The HOMO values of Pt(II) complexes were calculated from the oxidization potential onset, and LUMO values were determined by the difference between the HOMO and the corresponding optical band gap (Table 1).

The details of the compound's synthesis, ¹H and ¹³C NMR spectra of ligands and complexes (Fig. S1–S12, ESI[†]), and thermogravimetric analysis (TGA) curves (Fig. S13–S15) are given in the ESI.[†]

Photophysical properties

The UV-vis and photoluminescence (PL) spectra of **Pt1**, **Pt2** and **Pt3** are shown in Fig. 1. All these compounds displayed strong absorption below 300 nm, which was assigned to spin-allowed ${}^{1}\pi-\pi^{*}$ transition of the cyclometalating ligands. **Pt2** and **Pt3** exhibited moderate intense absorption bands in the 350–450 nm region, while **Pt1** showed an absorption cut-off up to 470 nm. Thus there is a red-shift of about 20 nm in the absorption spectrum of **Pt1** relative to those of **Pt2** and **Pt3**, which could be ascribed to low electro-negativity and high polarizability of the S atom in **Pt1**. A similar red-shift has been observed in the absorption spectrum of benzothiazole-based Ir(m) complexes in comparison with that of benzoxazole-based analogues.^{9e} The absorption bands with the wavelength over 400 nm of **Pt1–Pt3** could be attributed to the metal-to-ligand charge-transfer and spin–orbit coupling promoted ${}^{3}\pi-\pi^{*}$ states.^{13,14}

Upon photoexcitation at 420 nm, **Pt1**, **Pt2** and **Pt3** showed intense emission with vibronic progressions of 1199 cm⁻¹, 1208 cm⁻¹ and 1171 cm⁻¹, respectively. Considering that there is a red-shift in the absorption spectrum of **Pt1**, it is not surprising that **Pt1** showed a red-shift in phosphorescence in comparison with **Pt2** and **Pt3**. For example, the phosphorescence of **Pt2** has a



Fig. 1 Optical absorption and photoluminescence spectra of complexes Pt1, Pt2 and Pt3 in dilute dichloromethane solution at room temperature.

peak at 499 nm, which was blue-shifted by 24 nm relative to benzothiazole-based analogue **Pt1**. A red-shift by 8 nm was observed for complex **Pt3** relative to **Pt2**. Since the backbones of **Pt1–Pt3** are of very similar structural features, it can be deduced that the heteroatoms (S, O, and N) in tetradentate ligands **L1–L3** influenced the electronic structures and photophysical properties of the related Pt(n) complexes.

DFT calculations

In order to understand the photophysical properties of the emitters, density functional theory (DFT) calculations were performed for complexes **Pt1**, **Pt2**, and **Pt3** using Gaussian 09.¹⁵ The calculations were carried out using a B3LYP method with a basis set of 6-31G(d) for C, H, O, N and S atoms and a LANL2DZ basis set for a Pt atom. The rigid backbones in **Pt1–Pt3** are essentially coplanar, which allows the formation of an excimer in the solid state.

The orbital densities of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) are shown in Fig. S16 (ESI[†]). The HOMOs of **Pt1-Pt3** are in the range from -5.05 to -4.82 eV, and LUMOs are in the range from -1.52 to -1.70 eV. The similar composition and bonding pattern in these complexes help us to explain the small range of variation within the HOMO and LUMO energy levels. As estimated from the composition of the frontier orbitals, platinum made about 12–15% contribution to the HOMOs of **Pt1-Pt3**. The HOMOs of all these platinum(π) complexes primarily resided on the benzazole part, and obviously the major contributor was the phenoxide group. In **Pt1** the sulfur atom makes 3.13%

Table 1 Photophysical and electrochemical data obtained experimentally for the platinum(II) complexes										
Compou	ınd	λ_{abs}^{a} [nm]	$\lambda_{\rm em}{}^a$ [nm]	${\Phi_{\mathrm{p}}}^b$	$HOMO^{c} [eV]$	$LUMO^{d}$ [eV]	$HOMO^{e}$ [eV]	$E_{g}^{f}[eV]$		
Pt1		253, 297, 391, 428, 445	523, 558sh	0.26	-4.89	-2.26	-5.12	2.63		
Pt2		247, 286, 370, 401, 421	499, 531sh	0.25	-4.83	-2.02	-5.08	2.81		
Pt3		248, 289, 334, 372, 411	507, 539sh	0.41	-5.07	-2.35	-5.32	2.72		

^{*a*} Measured in CH₂Cl₂ at 293 K with a concentration of 10^{-5} M, sh = shoulder. ^{*b*} Measured in degassed CH₂Cl₂ relative to *fac*-[Ir(ppy)₃] ($\Phi_p = 0.4$). ^{*c*} Estimated from onset potentials using FeCp₂^{0/+} values of 4.8 eV below the vacuum level. ^{*d*} LUMO = HOMO + E_{g} . ^{*e*} HOMO values were calculated from UPS. ^{*f*} The optical band gap was estimated from the absorption spectra.

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X-ray crystal structure

A single crystal of **Pt3** was obtained by the slow evaporation method (Table S1, ESI[†]). The Pt atom in **Pt3** took a typical square planar coordination geometry with metal–ligand bond lengths in the range of 1.96–2.06 Å and the bond angles around the Pt atom in the range of $81.3-95.0^{\circ}$ (Fig. 2). Within **Pt3**, the pyridyl group, the benzimidazole motif and the benzene ring that contained C19 were essentially coplanar (this plane was defined as plane A). The phenoxide group was tilted by 21.1° with respect to plane A. The benzene ring of the phenoxide group and the bulky alkyl chain, 2-ethylhexyl, were located at each side of plane A, leading to the loose packing of these mononuclear motifs. In the solid state, **Pt3** molecules appeared in pairs with an intermolecular $\pi \cdots \pi$ distance of about 3.6 Å and a Pt…Pt distance of about 6.99 Å, which excluded any strong intermolecular Pt…Pt interaction.

Electroluminescence properties

To investigate the electroluminescence properties of **Pt1-Pt3**, OLEDs based on these dopants were fabricated with a normal



Fig. 2 Perspective view (top) and a dimeric structure (bottom) of Pt3 (all hydrogen atoms are omitted for clarity).

sandwiched structure. 1,4,5,8,9,11-Hexaazatriphenylene-hexacarbonitrile (HAT-CN) and 8-hydroxyquinolinolato lithium (Liq) were used as hole and electron injection layers, respectively. 1,1-Bis[4-[*N*,*N*-di(*p*-tolyl)-amino]phenyl]cyclohexane (TAPC) and 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB) were utilized as hole and electron transport layers, respectively. 4,4',4"-Tris(carbazol-9-yl)-triphenylamine (TCTA) was applied as the host material. The device configuration was ITO/HAT-CN (10 nm)/TAPC (40 nm)/ TCTA:dopant (*x* wt%, 15 nm)/TmPyPB (40 nm)/Liq (2 nm)/Al (120 nm) (dopant = **Pt1**, **Pt2**, and **Pt3**; *x* = 1, 3, 5, 10, and 15). The device data are summarized in Table 2.

Fig. S17 (ESI[†]) shows the EL spectra of complex Pt1 at various doping levels. At the doping level of 1 wt%, Pt1 emitted yellowish green light with a peak wavelength at 524 nm and a shoulder at 560 nm. Obviously, the EL spectra of Pt1 were dependent on the doping ratios. As the doping ratios of Pt1 were increased from 1 wt% to 15 wt%, a new emission band with the wavelength >600 nm appeared gradually and the CIE coordinates were shifted from (0.34, 0.62) to (0.44, 0.54). Thus at the high doping level Pt1 showed the excimer-based emission, which was typically red shifted and broader than the monomer-based emission.^{6a,g} Excimer based emission provides a powerful approach to achieve multiple-wavelength emission and white OLEDs with a single emissive material.^{7,16–18} Pt2 also showed excimer-based emission at a high doping level. Pt2 emitted yellowish green light with a peak wavelength at 504 nm and a shoulder at 536 nm with CIE coordinates of (0.28, 0.60) at the doping level of 1 wt%, and emitted greenish yellow light with CIE coordinates of (0.45, 0.51) at the doping level of 15 wt% (Fig. S20, ESI[†]). The EL spectra of Pt3 with different doping ratios in TCTA are shown in Fig. 3. Pt3, unlike Pt1 and Pt2, didn't develop any new emission band and the CIE coordinates were shifted slightly as the doping content was increased, which implied that the excimer-based emission was somehow suppressed greatly. Miskowski et al. suggested that strong Pt···Pt interaction and/or $\pi \cdot \cdot \pi$ interaction with an interplanar distance <3.5 Å would give rise to the low energy excimer emission.¹⁹ As revealed by X-ray crystallographic analysis, the introduction of the 2-ethylhexyl group into Pt3 eliminated the intimate metal \cdots metal interaction and strong $\pi \cdots \pi$ interaction within the dimeric structure, thus leading to the observation of the lack of excimer-based emission even at a high doping ratio. As expected from the observation of a red-shift in phosphorescence of Pt1, at the same doping level the CIE coordinates of Pt1 were red shifted in comparison with those of Pt2 and Pt3 (Table 2). So heteroatoms (S, N and O) also influenced the electroluminescence properties of this series of Pt complexes.

Highly electroluminescent OLEDs based on **Pt1-Pt3** have been achieved, and the turn-on voltages for these devices were found to be below 3.5 V. For **Pt1** and **Pt2**, the maximum device efficiencies (73.5 cd A⁻¹, 66.8 lm W⁻¹ and 19.8% for **Pt1**, and 62.0 cd A⁻¹, 56.2 lm W⁻¹ and 19.0% for **Pt2**) were obtained at the same doping level (5 wt%). For **Pt3**, the best device performance data were achieved at the doping level of 10 wt% with a peak η_c of 75.0 cd A⁻¹, η_p of 70.1 lm W⁻¹ and η_{EQE} of 21.4%. These efficiencies were among the highest for green/yellow 10

15

75.0

70.8

74.3

70.0

71.9

70.0

70.1

65.1

64.5

60.8

Table 2 EL performance of the Pt(II) complexes-doped OLEDs

Dopant	Dopant level [wt%]	$η_{c.max.}$ $η_{c.500}/μ$	/ /c.1000 ^a [c	d A ⁻¹]	$\eta_{ m p.max.}$ $\eta_{ m p.500}/\eta_{ m p.500}$	/ 1 _{p.1000} ^b [l1	$m W^{-1}$]	$\eta_{\mathrm{EQE.m}}$	_{ax.} /η ₅₀₀ /η ₁	₀₀₀ ^c [%]	λ _{em} [nm]	$\lambda_{ m sh}$ [nm]	CIE $(x, y)^d$	V _{turn-on} [V]
Pt1	1	58.5	51.6	46.2	45.4	35.8	27.6	15.3	13.5	12.0	524. 56	560	(0.34, 0.62)	3.4
	3	71.0	67.7	68.7	57.3	57.1	53.3	18.3	17.8	18.2	528	560	(0.35, 0.62)	3.3
	5	73.5	72.1	69.7	66.8	61.2	55.0	19.8	19.4	18.4	528	560	(0.36, 0.61)	3.3
	10	58.5	58.3	57.0	53.4	47.7	42.9	14.6	17.8	17.4	532	564	(0.39, 0.58)	2.6
	15	37.7	37.4	37.4	32.7	29.6	26.7	18.2	14.5	14.2	532	568	(0.44, 0.54)	3.2
Pt2	1	45.5	38.7	32.5	42.8	32.1	23.8	13.8	11.8	9.9	504	536	(0.28, 0.60)	2.9
	3	51.6	51.5	44.5	46.6	43.8	34.0	15.7	15.7	13.5	504	536	(0.29, 0.60)	2.8
	5	62	59.5	56.3	56.2	49.4	43.1	19.0	18.2	17.3	504	536	(0.32, 0.59)	2.8
	10	51	50.8	49.4	43.9	37.7	34.0	17.9	17.5	16.9	540	508	(0.39, 0.55)	3.1
	15	43.4	43.3	42.8	36.5	31.6	28.5	17.6	17.3	16.8	588	544, 508	(0.45, 0.51)	2.7
Pt3	1	58.0	54.0	46.9	52.6	44.4	35.4	16.3	15.1	13.3	512	544	(0.31, 0.61)	2.9
	3	60.4	59.3	56.6	50.9	49.5	43.4	16.9	16.6	15.8	512	544	(0.31, 0.61)	3.0
	5	66.0	63.8	63.0	54.1	54.1	49.3	18.5	17.9	17.6	512	544	(0.31, 0.61)	2.9

^{*a*} The maximum current efficiency ($\eta_{c,max}$), and current efficiencies ($\eta_{c.500}$ and $\eta_{c.1000}$) measured at a brightness of 500 cd m⁻² and 1000 cd m⁻², respectively. ^{*b*} The maximum power efficiency ($\eta_{p,max}$), and power efficiencies ($\eta_{p.500}$, $\eta_{p.1000}$) measured at a brightness of 500 cd m⁻² and 1000 cd m⁻², respectively. ^{*c*} The maximum external quantum efficiency ($\eta_{EQE,max}$), and EQES ($\eta_{EQE.500}$, $\eta_{EQE.1000}$) measured at 500 cd m⁻² and 1000 cd m⁻², respectively. ^{*d*} Commission Internationale de L'Eclairage coordinates measured at 5 mA cm⁻².

21.4

20.5

21.1

20.4

20.3

20.2

57.5

55.7



Fig. 3 The EL spectra of complex Pt3 with a current density at 5 mA cm $^{-2}$.

emitting OLEDs based on tetradentate Pt complexes, 3e,5,6a and also comparable with those for the yellow emitting OLEDs based on Ir(III) complexes.^{2h} The current efficiencycurrent density curves for Pt3 are depicted in Fig. 4. As the current density was increased, the current efficiency decreased gradually, which was ascribed to triplet-triplet annihilation and field-induced quenching effects.²⁰ As shown in Fig. 5, Pt3 exhibited a low efficiency roll-off at a brightness of 1000 cd m⁻² with an external quantum efficiency η_{EQE} of 20.3% (5.1% roll-off). While the EQE roll-off ratio from the peak value to that at a brightness of 1000 cd m^{-2} was 7.1% for Pt1, and 8.9% for Pt2. So the introduction of the 2-ethylhexyl group into Pt3 enhanced the emission quantum yield and diminished the efficiency roll-off ratios because the bulky chain discouraged the strong intermolecular interaction in the solid state.



512

516

544

548

Fig. 4 The current efficiency–current density curves for **Pt3** at different doping ratios.



Fig. 5 The EQE-luminance-current efficiency curves for **Pt3** at different doping ratios.

2.7

2.7

(0.33, 0.61)

(0.34, 0.61)

Conclusions

In summary, three Pt complexes (**Pt1–Pt3**) based on benzazolecontaining tetradentate ligands were successfully synthesized. The heteroatoms within the rigid ligands influenced the electronic structures and photophysical/electroluminescence properties of these Pt complexes greatly. High device performance was achieved by using **Pt1–Pt3** as emitters, and notably **Pt3** exhibited an excellent efficiency with the maximum η_c of 75.0 cd A⁻¹, η_p of 70.1 lm W⁻¹ and η_{EQE} of 21.4%. The bulky alkyl chain in **Pt3** suppressed the intermolecular interaction and eliminated the excimer-based emission, and thus was responsible for its high efficiency and stability.

Experimental

General information

¹H NMR spectra were recorded on a Bruker 400 MHz NMR instrument and ¹³C NMR spectra were recorded on an Agilent DD2-600 MHz NMR instrument. Mass spectra were recorded on a Thermo ISQ mass spectrometer using a direct exposure probe and MALDI-TOF mass spectra were recorded on a Bruker ultraflextreme MALDI-TOF spectrometer. UV-vis absorption spectra were recorded on a Cary 60 spectrometer (Agilent Technologies). PL spectra were recorded on a HORIBA Scientific FluoroMax-4 spectrofluorometer. Thermogravimetric analysis (TGA) was performed on a TA SDT 2960 instrument at a heating rate of 10 °C min⁻¹ under nitrogen. HOMO values were determined by Ultra-violet photoemission spectroscopy (Kratos Analytical Shimadzu Group Company). Cyclic voltammograms of these platinum complexes were recorded on a CHI600 voltammetric analyzer at room temperature in a 0.1 M tetrabutylammonium hexafluorophosphate solution under nitrogen gas protection.

X-ray crystallographic study

Crystal data for compound **Pt3** were collected on a Bruker APEX-II CCD diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å) at 296(2) K. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL crystallographic software package.²¹ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the molecule were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. A summary of the crystallographic data and structure refinement details is given in Table S1 (ESI⁺). The CCDC number is 1061613 for **Pt3**.

Device fabrication and measurements

OLED devices were fabricated through vacuum deposition on commercial ITO-coated glass substrates having a sheet resistance of 15 Ω per square. The ITO surface was ultrasonically cleaned with acetone, ethanol, and deionized water, then dried in an oven at 120 $^\circ C$ and treated by UV ozone for 15 min.

All layers were deposited under a base pressure of 2×10^{-6} Torr. The deposition rates and doping concentration of the films were monitored *in situ* by the calibrated thickness monitors. The typical evaporation rate for HAT-CN, organic

layers and Liq were 0.4–0.8, 2–3 and 0.2–0.5 Å s⁻¹, respectively. Finally, the Al electrode was evaporated (5 Å s⁻¹) through a shadow mask without breaking the vacuum.

The emitting area of each device was $3 \times 3 \text{ mm}^2$. Electroluminescence (EL) spectra, CIE coordinates and current-voltage (*I–V*) characteristics were measured using a constant current source (Keithley 2400s Source Meter) combined with a photometer (Photo Research PR 655 spectrophotometer).

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