## Aluminium–salen luminophores as new hole-blocking materials for phosphorescent OLEDs†‡

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The organic light-emitting diodes (OLEDs) employing complex [salen('Bu)<sub>4</sub>Al( $OC_6H_4$ -*p*- $C_6H_5$ )] (4) as a hole-blocking layer produced stable green EL emission of Ir(ppy)<sub>3</sub> irrespective of changing current density and showed higher brightness and device efficiency than the BAlq-based device.

Phosphorescent organic light-emitting diodes (PhOLEDs) based on heavy metal complexes have recently received great attention due to their high internal quantum efficiency, up to 100% of a theoretical value, from contribution of both singlet and triplet excitons for light-emission.<sup>1,2</sup> Nonetheless, PhOLEDs have a barrier, *inter alia*, to overcome: triplet excitons can diffuse to the adjacent layers due to their long lifetime,<sup>1a</sup> leading to undesired emission or quenching of light. Thus, the confinement of triplet excitons within an emitting layer (EML) is necessary to deploy phosphorescent emitters, which requires an additional hole-blocking layer (HBL) between an EML and an electron-transporting layer (ETL).<sup>2</sup> The HBL could also be advantageous to control of charge balance by blocking hole-diffusion from the EML into the ETL.

In order to achieve high device performance, such hole-blocking materials are required to have a deep highest occupied molecular orbital (HOMO) energy level, a large energy band gap, and a lowest unoccupied molecular orbital (LUMO) energy level close to that of an ETL. Hole-blocking materials that are developed up to date include quinolinol-containing complexes,<sup>3</sup> multi-phenylene systems,<sup>4</sup> oxadiazole or triazol-containing compounds,<sup>5</sup> phenan-throline derivatives,<sup>2,6</sup> and spiro-type diazafluorene systems.<sup>7</sup> Among them are 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, known also as bathocuproine (BCP),<sup>2,6,a</sup> and bis(2-methyl-8-quinolinolato)-mono(4-phenylphenolato)aluminium (BAlq)<sup>3</sup> that have been the commonly used hole-blocking materials. OLEDs employing BCP that has a deep HOMO energy level with a large energy band gap showed high efficiency but a short device lifetime due to low stability while OLEDs employing BAlq displayed

relatively low efficiency but a fairly long lifetime delivered by high stability.<sup>3b</sup> Since the lifetime is a key factor for device fabrication, it is still of great interest to search for new penta-coordinated aluminium systems as hole-blocking materials that can produce high efficiency of phosphorescent emitters in conjunction with a long lifetime. In this regard, we now set out to determine if the pentacoordinated aluminium systems based on Schiff-base salen [N, N'bis(3,5-di-tert-butyl-salicylidene)-ethylenediamine] can be utilized as promising hole-blocking materials. Although tetradentate-salen derivatives have been widely used as anchoring ligands in various inorganic and organometallic fields such as catalysis,8 sensors,9 and molecular magnets<sup>10</sup> owing to their strong chelating ability, facile introduction of various subsitituents and easy synthesis, the photophysical properties and further applications to the OLED materials of metal-salen compounds have rarely been investigated.9a,11 The only example of the use of bis(salen)Zn as an emitting material has recently been reported.<sup>12</sup> Herein, the brief accounts of the synthesis, structure, and novel OLED characteristics of salen-based aryloxy aluminium complexes 1-4 as hole-blocking materials are described.

Overall synthetic procedures for 1–4 are outlined in Scheme 1. Salen ligand was prepared by the reaction of 3,5-di-*tert*-butyl-2hydroxybenzaldehyde and ethylenediamine in a 2 : 1 molar ratio as reported previously.<sup>13</sup> Treatment of the salen with trimethylaluminium afforded the precursor<sup>14</sup> that in turn gave the desired penta-coordinated aluminium complexes 1–4 in 72–80% yield as yellow solids in the presence of the corresponding phenol.<sup>15</sup>



Scheme 1 Synthesis of the salen-based aluminium complexes.

The molecular structure of complex **4** illustrated in Fig. 1 reveals distorted penta-coordination geometry around Al ranging between trigonal bipyramidal and square pyramidal. Geometry analysis with the index of the degree of 'trigonality'  $\tau = (\beta - a)/60$  ( $\tau = 0$  for perfectly square pyramidal geometry and  $\tau = 1$  for perfectly trigonal bipyramidal geometry)<sup>16</sup> for **4** affords a  $\tau$  value of 0.61, indicating that the coordination geometry of **4** has a more trigonal bipyramidal nature. The Al–O3 bond length [1.7609(16) Å] and the Al–O3–C33 [136.49(14)°] angle of the

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<sup>†</sup> Crystal Data for **4**: C<sub>44</sub>H<sub>55</sub>AlN<sub>2</sub>O<sub>3</sub>,  $M_w$  = 686.88, monoclinic,  $P2_1/c$ , a = 20.263(8), b = 11.792(4), c = 18.060(9) Å, a = 90.00, β = 114.585(12), γ = 90.00°, V = 3924(3) Å<sup>3</sup>, Z = 4, T = 293(2) K, measd reflns = 22 087, unique reflns = 8569,  $R_{\rm int}$  = 0.0482, reflns used for refinement = 8569, R1 = 0.0522, wR2 = 0.1137. CCDC reference number 656227 (**4**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b717754b

<sup>‡</sup> Electronic supplementary information (ESI) available: Syntheses and characterization for 1–4, X-ray data for compound 4, and fabrication of OLEDs. See DOI: 10.1039/b717754b



**Fig. 1** Molecular structure of 4.† Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Al–O1 1.7900(17), Al–O2 1.7763(16), Al–O3 1.7609(16), Al–N1 1.9848(19), Al–N2 2.0093(19), O3–C33 1.339(3), O1–Al–O2 94.53(7), O1–Al–O3 97.33(8), O2–Al–O3 118.31(8), N1–Al–O1 89.26(8), N1–Al–O2 129.65(8), N1–Al–O3 110.86(8), N2–Al–O1 166.18(8), N2–Al–O2 88.18(7), N2–Al–O3 93.28(8), N2–Al–N1 78.66(8), C33–O3–Al 136.49(14).

Al–aryloxide moiety are comparable to those found in the similar (salen)Al( $OC_6H_2Me_3$ -2,4,6) compound.<sup>17</sup>

All the complexes 1-4 are air-stable both in the solid and solution states. Penta-coordinated aluminium complexes containing salen tend to show low chemical stability and readily dissociate into other species in the air or in the presence of Lewis base especially when an alkyl or halide unit is employed as an ancillary ligand.<sup>18</sup> Such enhancement of stability can be ascribed to the presence of tert-butyl groups in the salen ligand and aryloxide ancillary ligand, affording the encapsulation of the metal center and stronger bonding with Al, respectively. In addition, the presence of tert-butyl groups increases the solubility of the complexes in common organic solvents. The increased chemical stability seems to lead to the increased thermal stability as indicated by 5 wt% decomposition temperatures,  $T_{d5}$  of 230, 270, 280 and 330 °C for complexes 1-4, respectively. These results also indicate that thermal stability can be modified dramatically by change of the ancillary ligand.

The absorption and emission spectra of complex **1** in chloroform are shown in Fig. 2 and the spectroscopic and energy level data for all the complexes are summarized in Table 1.<sup>19</sup> The spectroscopic properties of complexes **1–4**, the absorption and emission max-

Table 1 Spectroscopic and energy level data for complexes 1-4

Complex	$\lambda_{abs}{}^{a}/nm (\log \varepsilon)$	$\lambda_{\rm em}{}^a/{\rm nm}~(\eta_{\rm rel})^b$	HOMO <sup>c</sup> /eV	LUMO/eV
1	363 (4.01)	480 (0.35)	5.3	2.4
2	364 (3.98)	479 (0.41)	5.0	2.1
3	366 (3.92)	479 (0.40)	5.4	2.5
4	364 (4.04)	480 (0.31)	5.2	2.3

<sup>*a*</sup> Chloroform solution  $(1.0 \times 10^{-5} \text{ M})$ . <sup>*b*</sup>  $\eta_{\text{rel}}$  is the relative PL efficiency with respect to that (0.55) of quinine sulfate.<sup>20 c</sup> HOMO energy levels were determined from the oxidation potentials measured by cyclic voltammetry in CH<sub>2</sub>Cl<sub>2</sub>.



Fig. 2 UV-Vis absorption and photoluminescence (PL) spectra of 1.

imum wavelengths at 364 nm and 480 nm, respectively, are very similar regardless of the type of the ancillary aryloxy ligand. The fluorescence quantum efficiencies of complexes 1-4 are in the range 0.31–0.41.<sup>20</sup> The HOMO–LUMO energy gaps of all complexes 1-4 were estimated as 2.9 eV from the absorption edges of the optical absorption spectra, indicating that the ancillary ligand attached to the aluminium–salen luminophore has little effect on the energy band gap. On the other hand, the HOMO energy levels are determined from the cyclic voltammetric oxidation potential<sup>21</sup> and thereby the LUMO energy levels are slightly dependent on the ancillary ligand.

In order to evaluate the OLED characteristics of the foregoing salen-based aryloxy aluminium complexes as hole-blocking materials, **4** was selected since it shows the highest thermal stability and has the HOMO–LUMO energy levels comparable to those (5.2–2.2 eV HOMO–LUMO levels) of BAlq. Two OLEDs (OLED-**4** and OLED-BAlq) were fabricated by vacuum deposition with the structure of ITO (anode)/CuPc (HIL, 10 nm)/ $\alpha$ -NPD (HTL, 40 nm)/8wt% Ir(ppy)<sub>3</sub> in CBP (EML, 50 nm)/**4** or BAlq (HBL, 10 nm)/Alq<sub>3</sub> (ETL, 30 nm)/LiF (EIL, 1 nm)/Al (cathode, 100 nm) (CuPc = copper phthalocyanine, HIL = holeinjection layer,  $\alpha$ -NPD = 4,4'-bis(*N*-1-naphthyl-*N*-phenylamino)biphenyl, HTL = hole-transporting layer, CBP = 4,4'-bis(*N*carbazolyl)biphenyl, Ir(ppy)<sub>3</sub> = tris(2-phenyl-pyridine)-iridium, Alq<sub>3</sub> = tris(8-hydroxyquinolinolato)aluminium, EIL = electroninjection layer).

Both devices emitted bright green light contributed only from Ir(ppy)<sub>3</sub> and their EL spectra were not significantly changed upon varying the applied voltage. The CIE color coordinate was changed slightly from (0.27, 0.64) to (0.27, 0.63) in the case of OLED-BAlq as the current density increased from 10 mAcm<sup>-2</sup> to 100 mAcm<sup>-2</sup> while OLED-4 maintained the constant CIE color coordinate at (0.27, 0.63). These results indicate that complex 4 functions as a stable hole-blocking layer material. Fig. 3a displays current density as a function of applied voltage and luminance as a function of current density. The turn-on voltages of OLED-4 and OLED-BAlq are 5.4 and 5.2 V, respectively. The current density and the brightness of OLED-4 were measured as 70 mAcm<sup>-2</sup> at 13 V and 16 200 cdm<sup>-2</sup> at 100 mAcm<sup>-2</sup>, respectively. OLED-BAlq showed a current density of 116 mAcm<sup>-2</sup> and a brightness of 13000 cdm<sup>-2</sup> under the same conditions. As shown in Fig. 3b, OLED-4 gave a luminous efficiency ( $\eta_L$ ) of 17.1 cdA<sup>-1</sup> and a power efficiency ( $\eta_p$ ) of 4.7 lmW<sup>-1</sup> at 20 mAcm<sup>-2</sup> that can be compared



**Fig. 3** (a) J-V-L characteristics and (b) luminance and power efficiency as a function of current density of OLED-4 ( $\triangleright$ ) and OLED-BAlq ( $\blacksquare$ ).

with  $\eta_{\rm L} = 12.3 \,\text{cdA}^{-1}$  and  $\eta_{\rm p} = 3.6 \,\text{lmW}^{-1}$  for OLED-BAlq. Overall, complex 4 led to much improved OLED performance with higher brightness and efficiency as compared to BAlq as hole-blocking materials.

In summary, a set of new stable aluminium–salen luminophores was developed and tested selectively as hole-blocking layer materials for a green phosphorescent OLED. The OLED-employing complex **4** produced stable green EL emission of Ir(ppy)<sub>3</sub> irrespective of changing current density and showed higher brightness and device efficiency than the BAlq-based device, implying that aluminium–salen based luminophores would constitute a promising class of hole-blocking materials for phosphorescent OLEDs. Currently, various synthetic modifications based on molecular orbital calculations are in progress to establish the scope of salenbased aluminium complexes as OLED materials.

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