Strongly luminescent binuclear aluminium chelate with polymer-like molecular packing and solution-processibility†

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A binuclear aluminium(III) chelate with rigid and flexible mixed ligands has been synthesized and structurally characterized, which exhibits polymer-like molecular packing and solution-processiblity, as well as high photoluminescence quantum yield for organic light-emitting diodes (OLEDs); with this new compound as the emissive and host layer, the multi-layer OLEDs prepared *via* low-cost spin-coating showed encouraging performance.

Since 1987, when the first organic light-emitting diodes (OLEDs) were fabricated from tris(8-hydroxyquinoline) aluminium(III) (Alq_3),[1] Alq_3 has been regarded as one of the most popular and effective molecules and its derivatives have attracted a great deal of attention. Many derivatives of Alq_3 have been investigated as emitter materials, including those with substitution of the metal ion with other metals[2] and substitution of the 8-quinolinol ligand[3] and introduction of other ligands.[4] The routine metal chelates are generally processed by vacuum evaporation. This method, whilst well proven, has potential commercial disadvantages for large area full color displays.[5] It is desirable to design and synthesize solution-processible small molecules, which could open up the possibilities of fabricating small molecule OLEDs (SMOLEDs) in a way similar to polymer light-emitting diodes (PLEDs) by low cost solution techniques.

Several approaches address this issue, including the developments of large dendritic molecules,[6] oligomers,[7] and spiro-molecules.[8] However, much less attention has been directed toward solution-processible organic metal chelates, while it is well known that organic metal chelates play an important role in SMOLEDs. Recently, Elschner *et al.*[9] and Cheng *et al.*[10], respectively, reported that some gallium complexes and a sulfonamide-substituted aluminium quinolate could be spin-coated to fabricate OLEDs. However, fabrication of SMOLEDs through solution-processing are still challenging. In our research, we focused on metal(III) chelates based on tridentate Schiff base ligands, which have proved to be of high luminescence.[11] The reported metal chelates provide evaporated films with reduced pinhole and roughness comparing with Alq_3. Herein, we describe a binuclear aluminium chelate with mixed ligands of β-diketone and the tridentate Schiff base, $[Al(saph)DPM]_2$ bis[(salicylidene-*o*-aminophenolato)-(dipivaloylmethane)aluminium(III)], which possesses particular molecular structure and polymer-like molecular packing and solution-processibility, that is very different from conventional metal chelates of this type.

$[Al(saph)DPM]_2$ was prepared through a complexing reaction in the ethanol solution of $AlCl_3$, saph (salicylidene-*o*-aminophenol), and DPM (dipivaloylmethane) at a 1 : 1 : 1 molar ratio. The molecular structure was characterized by ^1H NMR spectroscopy, FT-IR spectroscopy, and elemental analysis. The solid state structure was elucidated by a single-crystal X-ray diffraction analysis on the crystal selected from the sublimed product.‡

Fig. 1 shows the X-ray crystal structure of $[Al(saph)DPM]_2$. This chelate has a well-defined dimeric structure with two distinct Al^{3+} ion centers. And each Al atom is hexacoordinate with five oxygen atoms and one nitrogen atom and the angles around aluminium approximately octahedral. Two Al atoms are involved in bridging through the phenolato oxygen atom of saph. This dimeric structure is further stabilized by strong $C–H\cdots\pi$ intramolecular interactions of $C(1)–H(1A)\cdots\pi$ and $C(1A)–H(1AA)\cdots\pi$ (3.10Å). As shown in Fig. 1, it was found that the tridentate Schiff base ligand, saph, is locally disordered, which was marked by N(1), C(18) and N(1′), C(18′). Each saph has two sets of positions, with 50% occupancy for each set of positions. This is just because the distinct bonding modes of bridging oxygen and terminal oxygen are not interchangeable by simply reorienting the molecule. The origin of the disorder could be due to the coexistence of different structural isomers in the crystal lattice.[12]

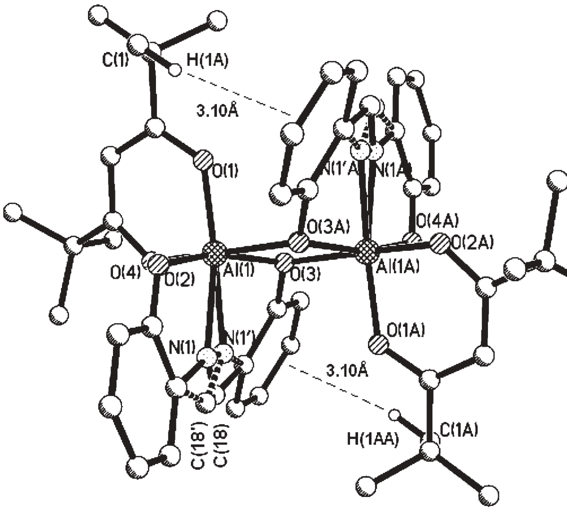

Fig. 1 The perspective plot of $[Al(saph)DPM]_2$. The disordered saph is shown by N(1′) and C(18′) with dashed lines as the bonds to the other atoms. The other hydrogen atoms are omitted for clarity.

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Interesting packing and intermolecular interactions have been observed in the crystal lattice. As shown in Fig. 2, there are two different interactions between the neighboring molecules. One is the moderate π–π stacking interaction (3.77 Å), which occurs between the phenyl/phenyl rings of saph ligands. Such π–π links generate an extended one-dimensional chain along the *b* direction. The other is the C–H$\cdots\pi$ intermolecular interactions (3.22 Å) between the *t*-butyl groups of one molecule and the phenyl rings of the neighbouring one, leading to an aggregation of the hook-like *t*-butyl groups pointing toward each other. This C–H$\cdots\pi$ interaction thus interlaces with π–π stacking chains, resulting in a packing motif quite similar to the conformation of polymer chains, thus suppressing intermolecular aggregation. This polymer-like packing *via* intermolecular interactions in solid [Al(saph)DPM]$_2$ might be conducive to film formation by the solution process.

[Al(saph)DPM]$_2$ can be dissolved in tetrahydrofuran (THF) and common alcohols. The complex forms good optical quality thin films from solutions. Table 1 shows the AFM characteristics of thin films formed by spin-coating or evaporation, with Alq$_3$ and poly(9-vinylcarbarzole) (PVK) films as the references. Although Alq$_3$ can also be easily dissolved in organic solvents, it has to be sublimed and cannot be deposited from solution, otherwise the underlying hole transporting layer would redissolve.[9] The only solvents that will not dissolve the triarylamines layer or PVK are water or common alcohols. In contrast, no matter what method, [Al(saph)DPM]$_2$ could form uniform and pinhole-free films, even through spin-coating from methanol solution. The root-mean-square of the roughness (RMS) and P–V values are almost half smaller than that of Alq$_3$, and comparable to that of PVK film.

Table 1 The AFM characteristics of the thin films

Material	Method	Solvent	RMS/nm	P–V/nm
Alq$_3$	Evaporation	—	0.88	12.39
[Al(saph)DPM]$_2$	Evaporation	—	0.51	5.38
[Al(saph)DPM]$_2$	Spin-coating	Methanol	0.25	8.61
[Al(saph)DPM]$_2$	Spin-coating	THF	0.19	6.23
PVK	Spin-coating	THF	0.21	2.54

Fig. 3 shows its absorption and emission spectra of spin-coated thin films. The lowest-energy absorption band centered at 418 nm should be assigned to the combination of the π–π* and *n*–π* transitions of the chelated saph.[11c] It exhibits intensive green luminescence and the same PL spectrum both in solution and in thin film. The quantum efficiency of this emission (0.639 in DMF) is high, and 5.5 times that of Alq$_3$, which should be ascribed to largely minimized non-radiative rates due to the rigid binuclear structure.

Such high luminescence along with its solution-processibility makes [Al(saph)DPM]$_2$ a good emitter for solution-processed SMOLEDs. It shows high solubility in methanol, which is a

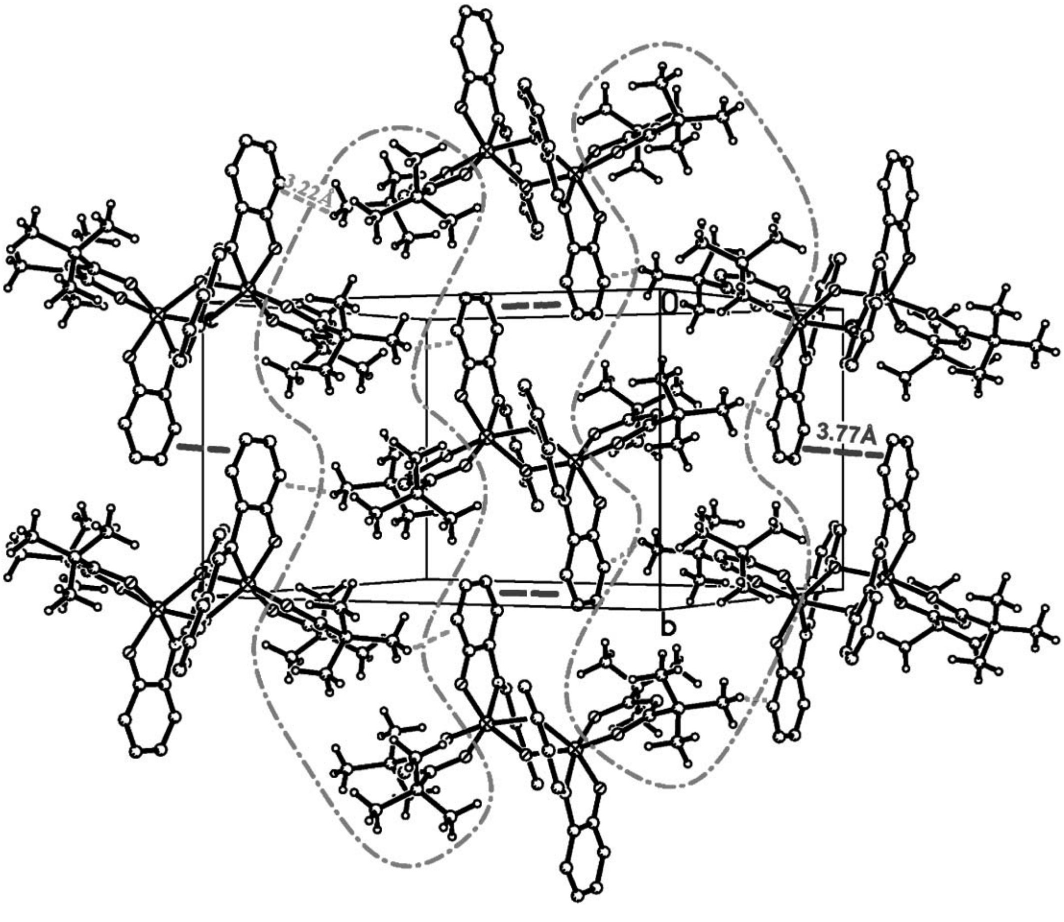

Fig. 2 Crystal packing of [Al(saph)DPM]$_2$, showing intermolecular π–π stacking of the ligands (long dashes), C–H$\cdots\pi$ interactions (short dashes) and the physical aggregation of the *t*-butyl groups (encircled within the dotted-and-dashed lines). The disordering was omitted for clarity.

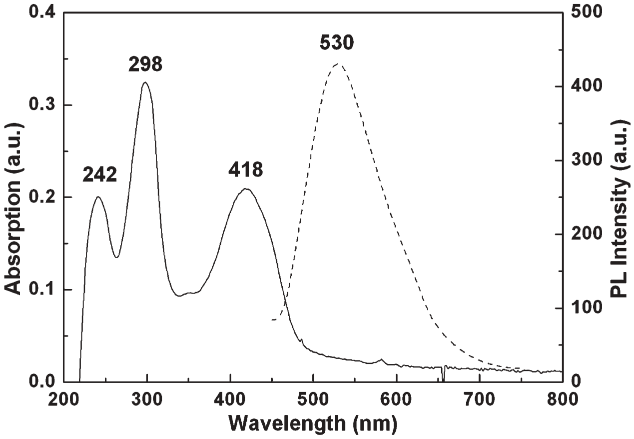

Fig. 3 UV-Vis absorption (solid line) and emission (dashed line) spectra of $[Al(saph)DPM]_2$ film by spin-coating from THF solution.

poor solvent for most OLEDs materials, providing a possibility of fabricating high-performance multi-layer devices by a subsequent spin-coating process. Two bilayer devices with PVK : *N,N′*-diphenyl-*N,N′*-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD, 1 : 1 weight) as the hole-transporting layer, $[Al(saph)DPM]_2$ or $[Al(saph)DPM]_2$:rubrene (1%) as the emissive layer, were fabricated by successive spin-coating. The undoped device gave strong green emission from $[Al(saph)DPM]_2$ with a maximum brightness of 2810 cd m^{-2} at 20 V. The peak efficiency is 0.5 cd A^{-1}, which is higher than the previous report by Elschener *et al.*[9] The doped device gave the typical emission of rubrene and improved performance. The maximum brightness is 2900 cd m^{-2} at 14 V, indicating the efficient energy transfer from $[Al(saph)DPM]_2$ to rubrene. The peak efficiency is 1.4 cd A^{-1}, which is almost twice higher than that of the undoped one. Despite the fact that their current performances are inferior to those prepared using evaporated Alq_3 (2000 cd m^{-2} at 12–15 V with peak efficiencies 2–3 cd A^{-1} in undoped devices), we note that the device structure has the potential for further optimization. For example, the use of Li-based cathodes, proper control of spin-coating conditions, optimization thickness of organic layers, can result in a reduction of operating voltage and increased quantum efficiency.

In conclusion, we report a binuclear aluminium heteroleptic chelate with mixed ligands, which successfully combines solution-processibility with high luminescence quantum efficiency. It exhibits particular molecular structure and chain-like molecular packing in the solid state, shows potential as the active layer for multilayer SMOLEDs by low-cost solution techniques.

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Notes and references

‡ **Crystal data**: $[Al(C_{13}H_9NO_2)(C_{11}H_{19}O_2)]_2$, $M = 842.90$, monoclinic, $a = 13.4499(9)$, $b = 10.5525(7)$, $c = 15.9848(11)$ Å, $\alpha = 90.00$, $\beta = 93.351(2)$, $\gamma = 90.00°$, $U = 2264.8(3)$ Å^3, $T = 295 \pm 2$ K, space group $P2_1/n$ (No. 14), $Z = 2$, μ(Mo-Kα) = 0.119 mm^{-1}, 12288 reflections measured, 3989 unique (R_{int} = 0.035). The final $wR(F2)$ was 0.1391 (all data). CCDC 197758. See http://dx.doi.org/10.1039/b506907f for crystallographic data in CIF or other electronic format.

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