

# A blue electroluminescent molecular device from a tetranuclear zinc(II) compound $[\text{Zn}_4\text{O}(\text{AID})_6]$ (AID = 7-azaindolate)

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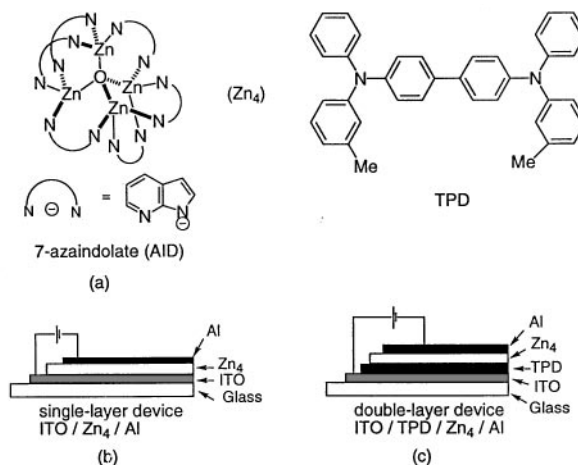
Received (in Cambridge, UK) 7th July 1998, Accepted 23rd September 1998

A tetranuclear zinc(II) compound with 7-azaindolate (AID) as a bridging ligand exhibits an intense blue emission at 425 nm with a quantum yield of 0.21 in acetonitrile solution at room temperature; a blue-light emitting diode based on the  $\text{Zn}_4$  complex as the active emitting layer attains an EL efficiency of 0.25% and brightness of  $88 \text{ cd m}^{-2}$  at 7.1 V driving voltage with current density of  $10 \text{ mA cm}^{-2}$ .

The search for new bright blue UV-luminescent metal–ligand compounds is of growing importance in the development of light emitting diode (LED) technology.<sup>1–3</sup> In this regard, polynuclear  $d^{10}$  metal complexes are of interest since these compounds are strongly emissive under UV irradiation, and the emission energies can span over a broad spectral range [400–700 nm].<sup>4,5</sup> Previously, we and Peng reported the preparation and crystal structure of a tetranuclear zinc(II) compound  $[\text{Zn}_4\text{O}(\text{AID})_6]$ , here denoted as  $\text{Zn}_4$ , with 7-azaindolate as a bridging ligand.<sup>6</sup> This compound has the following desirable features that enable it to be a good advanced material for blue LED device fabrication: it can be easily prepared and is stable to air and moisture. Our recent studies revealed that it has high thermal stability in air below 400 °C and displays an intense blue photoluminescence with a long lifetime and a high quantum yield at room temperature. The relevant photophysical data are summarised in Table 1. Herein is described a blue LED device with the  $\text{Zn}_4$  compound as the active emitting layer.

The  $\text{Zn}_4$  compound was prepared by the reaction of zinc(II) acetate with 7-azaindole in methanol, and its crystal structure had already been reported.<sup>6</sup> Schematic representations of the LED devices studied here are shown in Scheme 1. Initially a single-layer LED was fabricated by vacuum deposition of  $[\text{Zn}_4\text{O}(\text{AID})_6]$  ( $< 200 \text{ °C}$ ,  $2 \times 10^{-6} \text{ Torr}$ ) onto a glass substrate coated with indium–tin oxide (ITO; sheet resistance  $20 \text{ } \Omega \text{ } \square^{-1}$ ) to form a thin homogeneous film. The film thickness was found to be 700 Å, and the surface was examined by atomic force microscopy (AFM); the roughness of the surface is 3 nm (RMS amplitude) which is about +4.3% for the film thickness. The surface topology is stable up to 150 °C. The XRD pattern of the  $\text{Zn}_4$  thin film revealed a broad peak at  $2\theta = 15\text{--}30^\circ$ , which contrasts with the sharp peaks at  $2\theta = 10, 12$  and  $20^\circ$  observed for the crystalline powder sample. This indicates that the  $\text{Zn}_4$  compound in the vacuum deposited thin film is in an amorphous state. An aluminium cathode (thickness  $\approx 2000 \text{ Å}$ ) was vacuum deposited on top of the  $\text{Zn}_4$  film at an evaporation rate of  $3\text{--}5 \text{ Å s}^{-1}$ . The substrate was kept at room temperature during the deposition. The active area of the LED is  $2 \times 2 \text{ mm}^2$ .

When the single-layer LED was forward biased with the ITO electrode at positive polarity, blue EL was observed. The EL spectrum (Fig. 1) resembles the PL spectrum of the  $\text{Zn}_4$  film



Scheme 1

suggesting that it originates from an excited state of  $[\text{Zn}_4\text{O}(\text{AID})_6]$ . However, the brightness of the single-layer device is only  $2.5 \text{ cd m}^{-2}$  at a driving voltage of 6.5 V and current density of  $10 \text{ mA cm}^{-2}$ . Because the  $\text{Zn}_4$  compound has a high ionisation potential of 5.1 eV [c.f. 4.8 eV for tris(8-hydroxyquinolino)aluminium ( $\text{Alq}_3$ )], a hole-transport material such as *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD, thickness  $\approx 100 \text{ Å}$ )<sup>7</sup> was introduced between the emitting  $\text{Zn}_4$  and the ITO layers to form a double-layer device as depicted in Scheme 1. The EL brightness and efficiency have thus been greatly enhanced.

Fig. 2 shows the current density–voltage and EL intensity–voltage characteristics of the double-layer LED. When the LED was forward biased with the ITO electrode at positive polarity, blue EL was observed. However, when the device was reverse

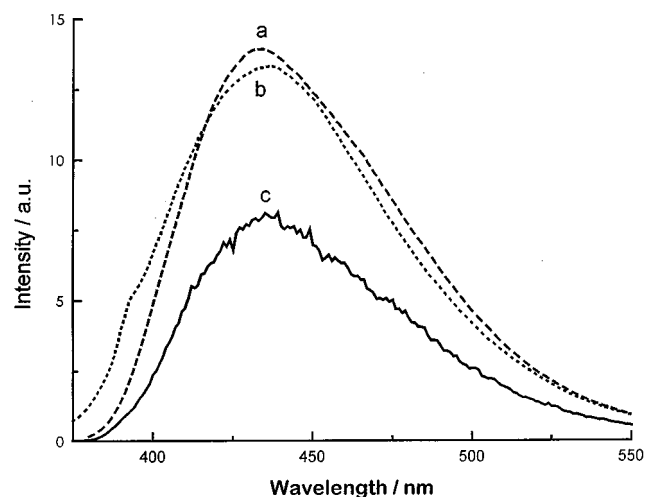


Fig. 1 (a) Solid state photoluminescence spectrum of  $\text{Zn}_4$ ; (b) photoluminescence spectrum of vacuum deposition  $\text{Zn}_4$  thin film; (c) electroluminescence spectrum of the single-layer device (ITO/ $\text{Zn}_4$ /Al).

Table 1 Photoluminescence data for  $[\text{Zn}_4\text{O}(\text{AID})_6]$  at room temperature

Solvent	$\lambda_{\text{max}}/\text{nm}$	Lifetime/ $\mu\text{s}$	Quantum yield
MeCN	425	0.09	0.21
$\text{CH}_2\text{Cl}_2$	427	0.08	0.19
MeCN glass (77 K)	423	0.11	—
solid state	433	0.05	—

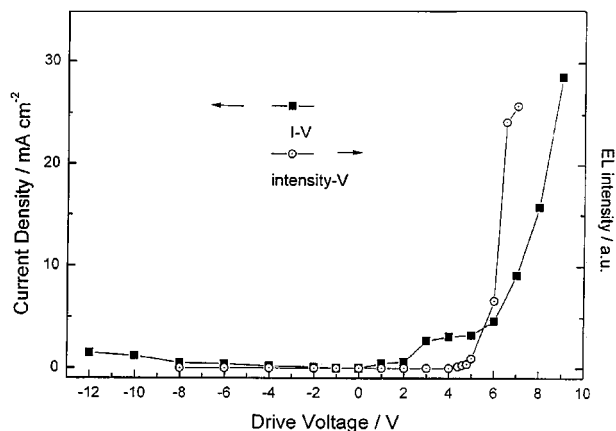


Fig. 2 Current density ( $I$ )-voltage ( $V$ ) and EL intensity-voltage characteristics.

biased, EL was not observed implying that it is not induced by the dielectric breakthrough of the layer system. The brightness of the device is about  $88 \text{ cd m}^{-2}$  at a driving voltage of 7.1 V and current density of  $10 \text{ mA cm}^{-2}$ , and an external EL efficiency of 0.25% (photons per electron) was found, which is 35 times higher than the single-layer device. The double-layer LED shows a rather low turn-on voltage of about 5 V, compared with  $>12 \text{ V}$  usually required for the  $\pi$ -conjugated polymer-based devices.

The EL spectrum of the double-layer LED shows two emission maxima at  $\lambda_{\text{em}} = 410$  and 430 nm (Fig. 3), and this is different from the PL spectrum. We suggest that one of the two emission peaks in the EL spectrum comes from an interface state originating from the TPD and the  $\text{Zn}_4$  layers; however, a precise explanation for this emission is not yet known.

Preliminary studies indicated that the present double-layer  $\text{Zn}_4$  LED device configuration is stable in open atmosphere. Because of its high thermal stability and high photoluminescence quantum yield, the  $\text{Zn}_4$  compound and its related derivatives may provide an alternative to the widely studied  $\text{Alq}_3$  compound for future development of LED devices.

We acknowledge support from the University of Hong Kong, the Hong Kong Research Grants Council and the Croucher Foundation.

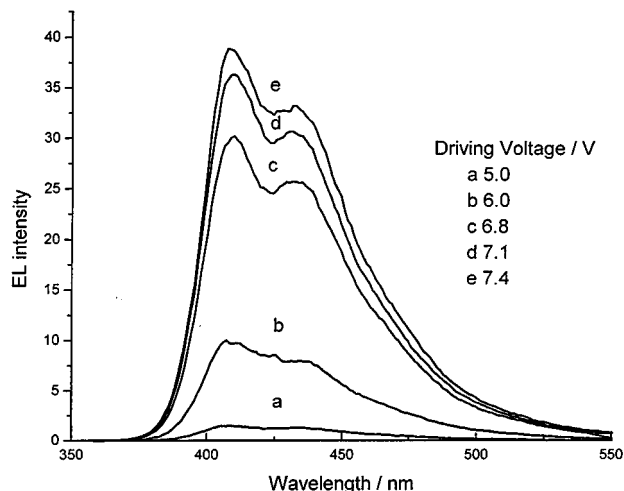


Fig. 3 EL spectra of the double-layer device at various driving voltages.

## Notes and references

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Communication 8/05236K