Letter

Light-emitting diode device from a luminescent organocopper(I) compound

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A highly luminescent tetranuclear copper(I) compound, $[Cu_4(C{\equiv}CPh)_4L_2]$ (Cu_4) [L = 1,8-bis(diphenylphosphino)-3,6-dioxaoctane], was used as an emitting material for fabrication of light-emitting diode (LED) devices. The Cu_4 doped poly(vinyl carbazole) device displays electroluminescence ($\lambda_{max} = 520$ nm) that is similar in energy to the photoluminescence recorded in dichloromethane. The device characteristics and mechanism of electroluminescence have been studied.

The use of luminescent inorganic binary compounds such as GaN and metal chalcogenides as light-emitting diode (LED) materials is well-documented. In contrast, related studies with luminescent metal-organic compounds such as Alq_3 [tris(8-hydroxyquinoline)aluminum] and its derviatives are still in their infancy.[1–3] In contrast to semiconductor nanocrystallites, polynuclear d^{10} metal compounds have well-defined molecular structures and recent studies have established their rich and diverse photoluminescent properties. Importantly, their excited state and physiochemical properties are tunable through variation of the metal atom and auxiliary ligands.[4–6] This, in principle, would allow the study of structure-property relationships in LED devices and provide a flexible entry to the fabrication process. Herein is described the luminescent complex $[Cu_4(C{\equiv}CPh)_4L_2]$ [L = 1,8-bis(diphenylphosphino)-3,6-dioxaoctane] as an advanced material for LEDs. This Cu_4 compound is air-stable, can be readily prepared from inexpensive starting materials,[7] and has an emission quantum yield comparable to that of the classic Alq_3 compound.[8] Moreover, the intramolecular Cu^I–Cu^I interaction may lead to a high carrier mobility and provide a new pathway for the carrier-transfer process. These advantages allow Cu_4 and its related complexes[6,9] to have useful optoelectronic applications.

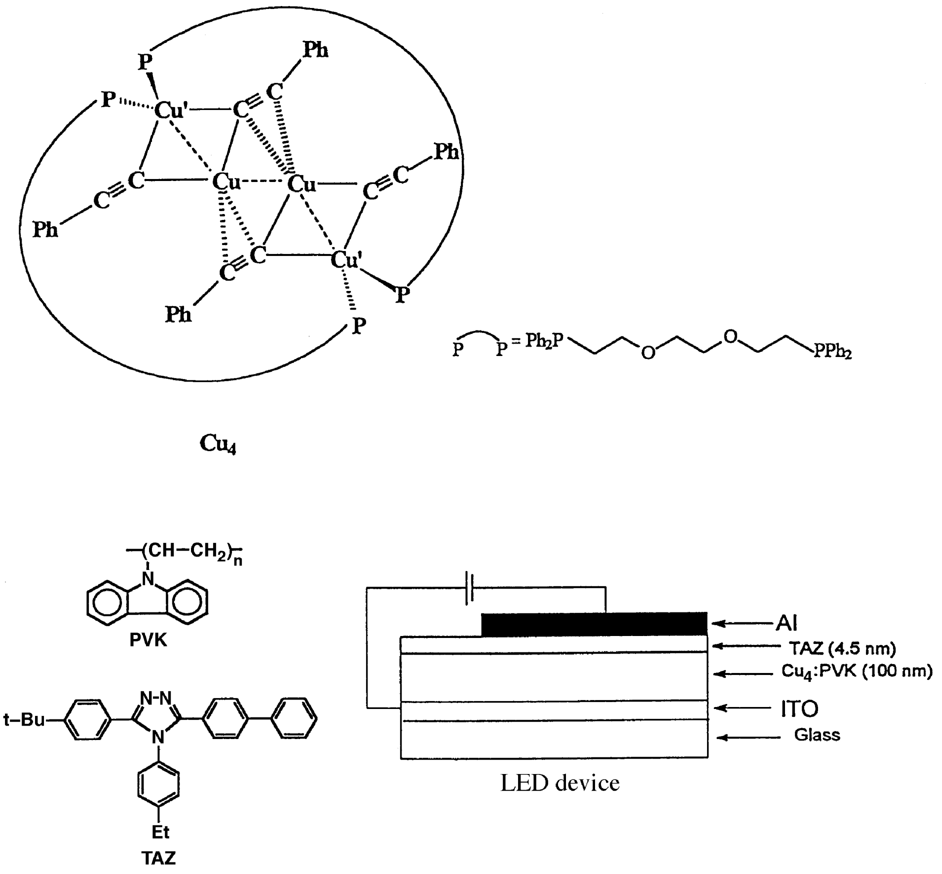

Fig. 1 Diagram showing the core structure of Cu_4 and the configuration of the LED device.

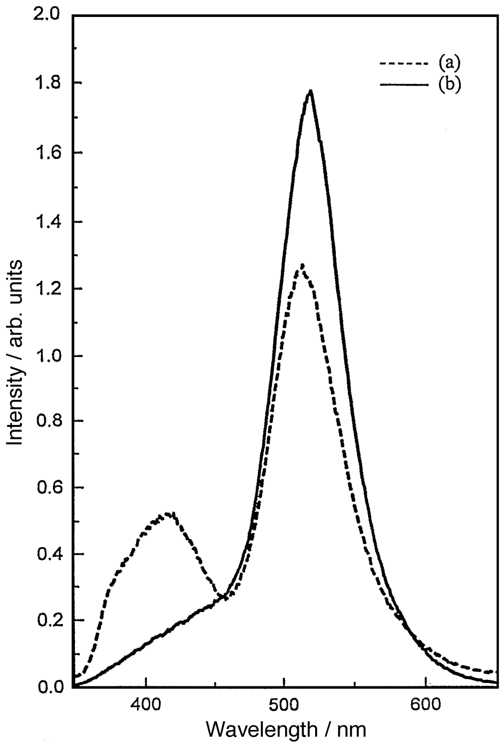

Fig. 2 (*a*) Photoluminescence spectrum of the Cu_4 : PVK film and (*b*) electroluminescence spectrum of the ITO/Cu_4:PVK/TAZ/Al device excited at 320 nm.

The core structure of the Cu_4 complex and the configuration of the LED device are depicted in Fig. 1. The complex has a zigzag Cu_4 core wrapped by two bridging phosphine ligands. It displays an intense low energy absorption at 408 nm ($\varepsilon = 7.8 \times 10^3$ M^{-1} cm^{-1}) that is attributable to an admixture of the metal-centered 3d → 4s/4p and $Cu^I \rightarrow \pi^*(C{\equiv}CPh)$ transitions. In room temperature dichloromethane solution, the complex exhibits an intense photoluminescence at 520 nm with a lifetime of 9.8 μs and quantum yield of 0.42. In solid state, the complex emits at 533 nm.

As the complex is non-volatile, a filming process using vacuum deposition cannot be used. We therefore immobilize it into a PVK polymer matrix that has a high hole drift mobility. In this work, two LEDs with the structures ITO/Cu_4 : PVK (1000 Å)/Al (single layer) and ITO/Cu_4 : PVK (1000 Å)/triazole derivative (TAZ 45 Å)/Al (double layer) were fabricated.† The TAZ layer, which transports electrons and blocks holes effectively, is generally used together with the Alq_3 electron-injection layer. However, the latter is not employed in our study since Alq_3 shows photoluminescence at a similar energy as that of the Cu_4 compound.

Fig. 2 shows the photoluminescence (PL) and electroluminescence (EL) spectra of the Cu_4 : PVK film measured at room temperature.‡ The PL spectrum of the Cu_4 : PVK (10 wt.% Cu_4) film shows two peaks at 516 and 420 nm (intensity ratio $I_{516}/I_{420} = 3$). The low energy emission (lifetime = 4.1 μs) originates from the triplet excited state of the Cu_4 complex, whereas the high energy emission (lifetime < 10 ns) is assigned to an exciplex emission of the carbazole groups in PVK.[10] In the EL spectrum, the emission intensity at $\lambda_{max} =$ 516 nm is much enhanced while the high energy band becomes a weak shoulder (intensity ratio $I_{516}/I_{420} = 10$). This can be explained by a higher formation efficiency of the triplet than that of the singlet state.[10]

The EL spectrum of a single layer Cu_4 device exhibits a weak emission with λ_{max} at 520 nm (driving voltage $\geqslant 12$ V), which is nearly identical with the PL spectrum of the complex measured in dichloromethane solution. This indicates that both the PL and EL originate from the same excited state.

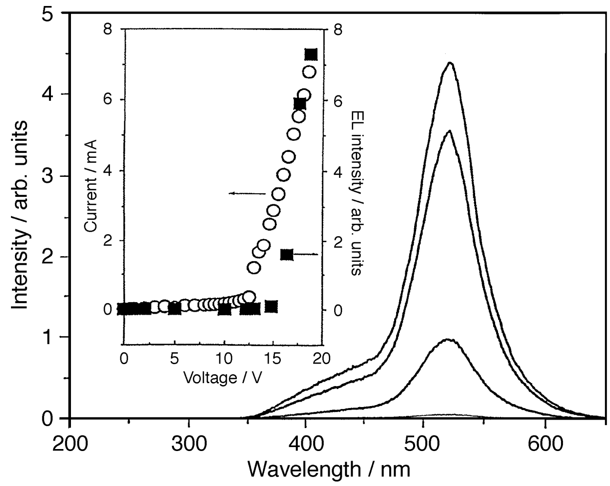

Fig. 3 Room temperature electroluminescence spectra of an ITO/Cu_4:PVK/TAZ/Al device at variable applied voltage. Insert: (○) current density and (■) EL intensity *versus* driving voltage.

For the double layer device, the turn-on voltage for EL (≈ 12 V) is similar to that of the single layer device but the emission efficiency is ten times higher for the same injecting current density. Presumably, the TAZ layer leads to a lower effective barrier for electron injection and/or a better confinement of holes to the emissive layer.[11]

The EL spectra of the double layer device at various applied voltages are depicted in Fig. 3. The insert graph shows plots of the current density and emission intensity *versus* the applied voltage. A non-linear relationship between the EL intensity and the current density is observed, which indicates a non-balanced charge injection in the device. When the applied voltage is less than 15 V, the injection barrier for the electrons in the TAZ layer is high, thus resulting in low EL efficiency. At high driving voltage, the electrons have sufficient energy to overcome the barrier and subsequently transport to the TAZ–PVK interface, where they combine with the holes to give the observed emission. The brightness at a current density of 20 mA cm^{-2} is *ca.* 50 cd m^{-2} and the estimated EL yield is 0.1%. We envisage that both the EL yield and the turn-on voltage can be further improved by using a low work-function cathode to enhance electron injection or materials with a higher electron affinity as the injection layer.

In this work, we have demonstrated the successful application of a polynuclear metal alkynyl compound for LED device fabrication. When compared to the d^8 poly-yne complexes of Pt^{II},[9] the d^{10} metal alkynyl complexes are advantageous because of their high luminescence quantum yields.[5] Thus, we envisage that polynuclear d^{10} metal alkynyl compounds, with their rich and diverse photoluminescent properties, have important applications in future development of LED technology.

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Notes and references

† LEDs were fabricated on indium–tin–oxide (ITO) coated glass substrates (sheet resistance 20 $\Omega/\square$), which were cleaned successively in ultrasonic baths of detergent, water, acetone, water and ethanol, and then dried under vacuum at 200 °C for 2 h. A thin emitting layer (typically 1000 Å) of Cu_4 : PVK (10 wt.% Cu_4) was formed by spin-coating a chloroform solution onto the ITO-coated glass substrate. TAZ (45 Å) was deposited on ITO at $\approx 2 \times 10^{-6}$ Torr ($\approx 2.67 \times 10^{-8}$ Pa) at a rate of ≈ 1 Å s^{-1}. An Al cathode (2000 Å) was vacuum deposited on top of these multilayer films at an evaporation rate of 3–5 Å s^{-1}. The substrate was kept at room temperature during deposition. The active area of the LEDs was 2×5 mm^2.

‡ Time-resolved luminescence decay was recorded on a boxcar averager using time-correlated counting methods. Excitation was monitored at 355 nm by a mode-locked Q-switched Nd : YAG laser with pulse width of 8 ns, frequency of 50 Hz and an integration power of 50 mW. All photophysical measurements were performed at room temperature.

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