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White OLED with a Single-Component Europium Complex

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A new direction for white organic light-emitting devices is shown, fabricated from a novel europium complex; this single component contains a double emission center of bluish-green and red, combined to a give a pure white emission (CIE x = 0.34 and y = 0.35).

Organic light-emitting devices (OLEDs) have become a major research area especially in industrial enterprises, where the drive for cheaper and more flexible displays is becoming a critical factor. The aim for improving color, stability, and manufacturing time and costs is constantly under competitive research.[1]

In designed full-color applications, it is necessary to have a set of red, green, and blue emitters with sufficiently high luminous efficiency and proper chromaticity.[2] After a decade of intensive research, organic materials for green and blue OLEDs with high luminescence, high efficiency, saturated emission, and practical lifetimes have been developed.[3,4] However, OLED technology is still yet to improve, especially when compared to other technologies such as liquid crystal displays (LCDs). One significant fallback is the cost of production, which is now also becoming a growing factor of concern especially against the rivalry of LCDs. The motivation for the present work has arisen from some studies in the literature. Kido et al. have investigated multicolored OLEDs from two lanthanide ions,[5], and Coppo et al. reported the use of one europium−iridium complex, which simultaneously emits blue and red to form the white OLED.[6] Recently, Giovanella et al. demonstrated their europium

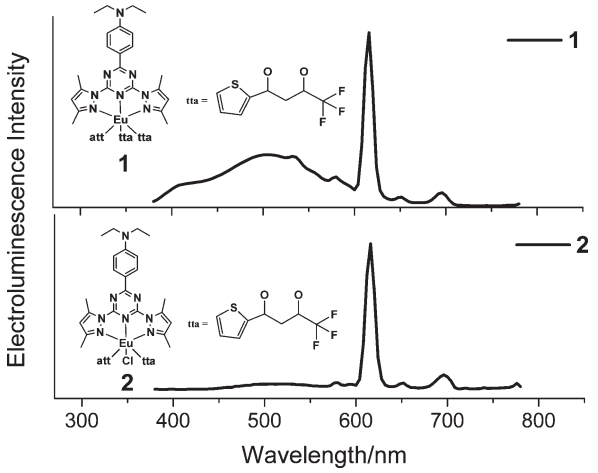

Figure 1. EL spectra of complexes **1** and **2** at 11 V.

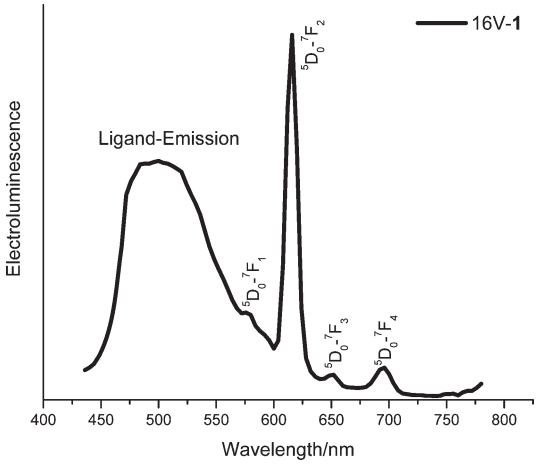

Figure 2. White EL spectra of complex **1** at 16 V with the blue ligand emission and red Eu f−f emission.

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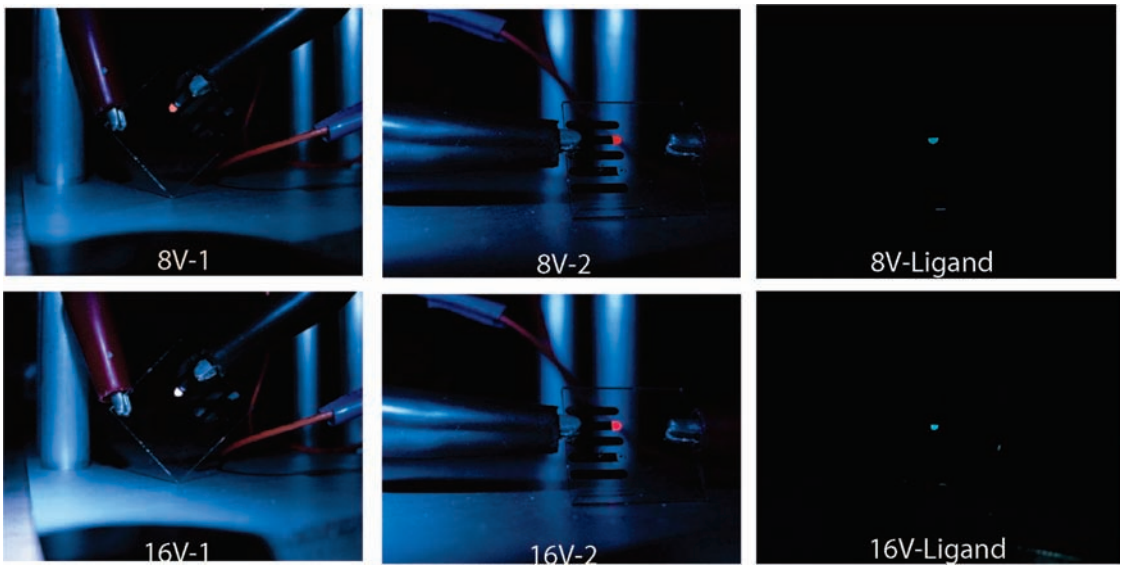

Figure 3. Photographs of the colors obtained with different voltages of 8 V (upper) and 16 V (lower). The turn-on voltage of these devices is at ~4 V. Complex **1** shows the white color (blue and green from the ligand and red from the europium f−f emission) in high voltage (start at ~12 V), and complex **2** gives the red f−f emission only. The ligands is the control and shows the blue-green emission with a peak at 505 nm, which comes from the ligand itself other than NPB and Alq_3. The solid-state emissions from the ligand, Alq_3, and NPB are demonstrated in the Supporting Information.

complex blend with poly(9,9-dioctylfluorene) in the device, which generated the white electroluminescence (EL).[7]

In this Communication, a new direction for white lanthanide OLED is shown, fabricated from a novel europium complex; this single component contains a double emission center of bluish-green and red, combined to give a pure white emission. With such single-component devices, three colors emit simultaneously, which is extremely rare. Therefore, lighter and thinner devices as well as a reduction in the manufacturing cost and time are possible. Two europium complexes have been shown, $[Eu(tta)_3 \cdot \mathbf{L}]$ (**1**) and $[Eu(tta)_2Cl \cdot \mathbf{L}]$ (**2**). Even though complex **1** has demonstrated a high quantum yield of the f−f emission with the direct energy transfer from a ligand singlet to $^5D_0$ (Eu) with various excitations in the solution state in our pervious literature[8] and also a high quantum efficiency, thermal stablity of complex **1** has been promoted for the oxygen sensor by Wolfbeis et al.[9] A new white OLED is shown that is fabricated from a novel organic europium complex, **1** (Figure 1). The single component contains a double emission center of bluish-green (ligand) and red f−f emissions (Eu) that are combined to give a pure white emission. A single-component device [indium−tin oxide (ITO)/NPB (50 nm)/CBP:Eu complex (10 nm)/BCP (30 nm)/Alq (20 nm)/LiF (1 nm)/Al (150 nm)] that emits the three colors simultaneously is rare, especially with the sharp fingerprint f−f emission band, and has the advantages of allowing the construction of lighter and thinner devices and reducing the manufacturing cost and time. Simultaneously, another analogus organic europium complex with the replacement of thenoyltrifluoroacetonate (tta) by chloride, **2**, is also newly synthesized and is used as the standard to solve the problem between the confusion of dopants (BCP) and complexes in the blue EL region.

The structure of our multilayer OLED is quite simple (Supporting Information). Our devices use an organic europium complex, which demonstrated different colors in complex **1** and only one red color in complex **2** with a change of the voltage. Our complex **1** is known to show a singlet−singlet energy transfer to give an intense characteristic red emission in both the solid and solution states.[9,10] Complex **2** is newly synthesized with a molecular structure as shown in Figure 1. The replacement of the tta group by chloride acts as an important control to confirm the white EL in complex **1**. All devices have a low turn-on voltage at 4 V (Table S2 and Figure S7 in the Supporting Information). Red EL can be observed in both complex **1** (until 13 V) and complex **2**; the four structured narrow visible bands are identified in their EL spectra at 594, 620, 650, and 700 nm of Eu, which are assigned to an electronic energy transition between $^5D_0 \rightarrow {}^7F_J$ (J = 1−4; Figures 1 and 2 and the Supporting Information)[11]

The device of complex **1** shows observation of the red emission at low voltage (4−13 V) and white emission at higher voltage (14−19 V). This color change is reversible, with the color emission being tunable by adjusting the voltage (Figure 3).[12] The device is relatively stable if the device limit is not exceeded, which is at 19 V; after this, the white phenomena will not be observed, and the green emission will dominate the EL spectrum because Alq_3 will be observed at 530 nm, which was previously blocked (Supporting Information). The EL spectrum of complex **1** with white EL at 16 V is shown in Figure 4. The corresponding CIE (Commission Internationale De L' Eclairage) coordinates of the white emission are $x = 0.34$ and $y = 0.35$.

To show that the emission at 505 nm was from phosphorescence of the ligand, EL studies of the ligand (Figure S7c in

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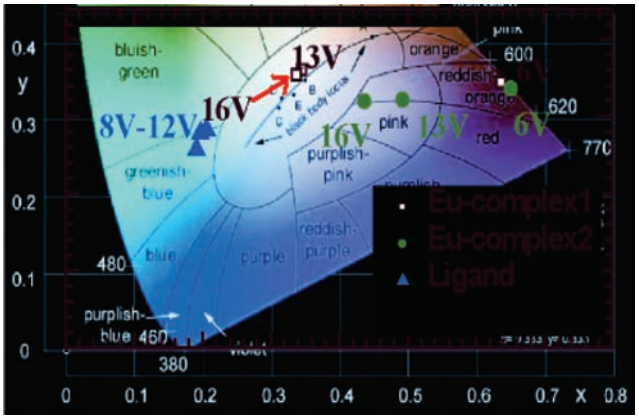

Figure 4. CIE graph of the trends of the color changes with voltage in the three samples (**1**, red; **2**, green; ligand **L**, blue).

the Supporting Information) and low-temperature emission experiments of the ligand, Alq_3, and NPB (Figure S8 in the Supporting Information) were carried out. The device constructed with only the ligand shows bluish-green emission, as observed in the EL spectrum in Figure 2. This corresponds with the broad peak at 505 nm found in **1**. Refer to photographs in Figure 4, which show no color change at high and low voltages for **2** and the ligand. An additional single-layer device with components of ITO, ligand, LiF, and Al has also been fabricated as a control experiment. Slightly blue EL can be found at ~9 V. This can prove that the blue EL from complex **1** in Figures 2−4 was induced by the ligand and not from the other organic materials used in the fabrication of the device such as CPB, Alq_3, or NPB. Low-temperature photoluminescence (PL) of the ligand, NPB, and europium complexes also demonstrated differences in their emission bands. The fabrication of a device from **2** also functions as a control experiment because it only shows red emission, which is different from the observed phenomena in **1**. Device **2** (Figure 2) even at a higher voltage of 16 V (Figure 3) only gives red emission.

From **2**, we also show that very slight structural modifications can have a drastic impact on the EL properties. By replacement of one of the tta groups in **1** with a chloride to give **2** (see the crystal structure), only the red emission is given in EL. There are also changes to its general photophysical properties, which can be seen in the UV and PL spectra, compared with those of **1**. The phenomena can be repeatedly observed with reversible color change (**1**), by adjusting the voltage; thus, the purity of the color emission is tunable.

Our new findings will offer a new direction to white OLED fabrications and perhaps address the area of low-cost production. We also show that very minor structural modifications can affect the properties of EL; this will allow us to fine-tune the efficiency and properties for future device fabrication and innovations.

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Supporting Information Available: Synthesis and device fabrications, EL and PL spectra of complexes, ligand and control experiment, UV−vis spectra, and CV data. This material is available free of charge via the Internet at http://pubs.acs.org.