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Review

Electroluminescence from europium(III) complexes

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Abbreviations: Alq_3, tris(8-quinolinolato) aluminum(III); AFTFBD, 2-acetylfluorene-4,4,4-trifluorobutane-1,3-dione; BCP, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline; BFPP, 2,3-bis(4-fluorophenyl)pyrazino[2,3-f] [1,10]phenanthroline; bpy, bipyridine; Bphen, 4,7-diphenyl-1, 10-phenanthroline; BTA, 4,4,4-trifluoro-1-phenyl-butane-1,3-dione; CBP, 4,4′-bis(9-carbazolyl)-2,2′-biphenyl; CE, current efficiency; CIE, Commission internationale de L′Eclairage; CPIP, 5-(5-carboxylatopyridin-2-yl)isophthalate; CRT, cathode ray tube; CT, charge transfer; CTL, carrier transporting layer; CV, cyclic voltammetry; D–A–A, donor–acceptor–acceptor; DBM, 1,3-diphenylpropane-1,3-dione; DCJTB, 4-(dicyanomethylene)-2-t-butyl-6-(1,1,7,7-tetra methyljulolidyl-9-enyl)-4H-pyran; DF, 4,5-diazafluorene; DPA, diphenylamine; DPEPO, bis(2-(diphenylphosphino)phenyl) ether oxide; DPPZ, 4,5,9,14-tetraazabenzotriphenylene; DPDBM, 1-(4-diphenylamino-phenyl)-3-phenyl-propane-1,3-dione; EFDPO, (9,9-diethyl-9H-fluorene-2,7-diyl)bis (diphenylphosphine)oxide; EL, electroluminescent; EMLs, emissive layer; EPIP, 3-ethyl-2-phenylimidazo [4,5-f] 1,10-phenanthroline; EQE, external quantum efficiency; ET, energy transfer; ETL, electron-transport layer; FDPO, 9,9-bis(diphenylphosphorylphenyl)fluorene; FMOs, frontier molecular orbitals; FRET, Förster resonance energy transfer; FWHM, full width at half maximum; HDLCD, high-definition liquid crystal display; HIL, hole-injecting layer; HOMO, highest occupied molecular orbital; HPIP, 2-phenylimidazo [4,5-f]1,10-phenanthroline; HTL, hole-transporting layer; IC, internal conversion; IET, intramolecular energy transfer; IP, imidazole fused phen; ISC, intersystem crossing; ITO, indium tin oxide; LMET, ligand-to-metal energy transfer; LMCT, ligand-to-metal charge transfer; LUMO, lowest unoccupied molecular orbital; MA, maleic acid; MMA, methyl methacrylate; m-MTDATA, 4,4′,4″-tris(3-methylphenylphenylamino)-triphenylamine; NPB, *N*,*N*′-bis-(1-naphthyl)-*N*,*N*′-bipheny-1,1′-biphe nyl-4,4′-diamine; NTA, nitrilotriacetate; Obpy, 2,2′-bipyridine mono *N*-oxide; OLED, organic light-emitting diode; Opy, pyridine *N*-oxide; OXD, 1,3,4-oxadiazole; PBD, 2-(4-biphenylyl)-5-(4-tert-butylphenyl-1,3,4-ox adiazole); PCzPIP, 2-phenyl-3-[3-(carbazol-9-yl)propyl]imidazo [4,5-f]1, 10-phenanthroline; PE, power efficiency; PEDOT:PSS, poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate); PF, polyfluorene; PFO, poly(9,9-dioctylfluorene); Phen, 1,10-phenanthroline; PL, photoluminescence; PLED, polymeric light-emitting diode; PLQE, photoluminescent quantum efficiency; PMMA, poly(methyl methacrylate); PMIP, tris(1-phenyl-3-methyl-4-isobutyryl-5-pyrazolone)(phenanthroline); PO, phosphine oxide; PVK, polyvinylcarbazole; PyBM, 2-prydinyl-benzimidazole; PyPhen, pyrazino[2,3-f][1,10]phenanthroline; sbf, 5-diaza-9,9′-spirobifluorene; TCPD, 1-[3,4,5-tris[4-(9H-carbazol-9-yl)butoxy] phenyl]-3-phenylpropane-1,3-dione; T_d, decomposition temperature; TEM, transmission electron microscope; T_g, glass transition temperature; THF, tetrahydrofuran; T_m, melting point temperature; TOPO, trioctylphosphine oxide; TPA, triphenylamine; TPBI, 1,3,5-tri(1-phenyl-1H-benzo[d] imidazole-2-yl)phenyl; TPD, tri-methylphenyl diamine; TPPO, triphenylphosphine oxide; TPTZ, 2,4,6-tripyridyltriazine; TTA, 2-thenoyltrifluoroacetonate.

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ABSTRACT

Lanthanide complexes are widely used as emitters for applications in the fields of bioimaging, molecular sensing, disease diagnosis, and optoelectronics. Particularly, the high luminescence efficiencies of these complexes make them attractive for electroluminescent display and solid-state lighting. As color purity and saturation are the most stringent criteria for red emission in display technology, europium(III) complexes featuring an emission peak centered at ~612 nm with a narrow bandwidth hold great potential as red-emitting materials. This review highlights the recent development of electroluminescent europium(III) complexes, with emphasis on correlations between molecular structures and optoelectronic performance. After a fundamental introduction on the optical and electrical properties of europium(III) complexes, efforts will be devoted toward the controlled synthesis and functionalization of molecules for improved charge injection/transportation, good processability, and enhanced emission efficiency.

1. Introduction

The choice of the emitters incorporated in the emissive layer (EML) of organic light-emitting diodes (OLEDs) dictates many photophysical processes, such as emission color tuning, photodegradation, radiative energy transition, as well as electrical modulation of the devices [1–3]. For example, the frontier molecular orbital (FMO) energy gap between an emitter and the charge-carrier transporting material deposited in adjacent layers directly determines the drive voltage of the device. In recent years, driven by pressing demands for lighting products, displays and other commercial applications, much research effort has centered on improving electroluminescent (EL) efficiencies and device stability. With these concerns in mind, researchers extensively investigate purely organic dyes and transition-metal complexes owing to their suitability as emitters for optoelectronic modulation. Nevertheless, in view of complex electronic transitions, the emission spectra of organic dyes and transition-metal complexes are asymmetric and broad with a large full width at half maximum (FWHM) of more than 3000 cm^{-1}. This precludes the use of these molecules to achieve high-definition display where high color purity and narrow emission band are essential [4–6].

Luminescent complexes comprising lanthanides are known as the emitters with high color purity owing to the characteristic *f–f* transitions of the lanthanides [7–13]. In most cases, lanthanide complexes have narrow emission bandwidths with FWHM smaller than 100 cm^{-1}, making possible the so-called monochromic emission. Therefore, lanthanide-based phosphors were often employed in video display terminals with high color saturation, such as cathode ray tube (CRT) and high-definition liquid crystal display (HDLCD) [14,15]. Fig. 1a shows the spectroscopic components of white emission from a commercial Lenovo ThinkVision™ L197 LCD display in which three primary colors were attributed to $^1G_4 \rightarrow {}^3H_6$ transition of Tm^{3+} for blue at ~430 nm, $^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+} for green at ~545 nm and $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} for red at ~612 nm. Therefore, one would intuitively expect the prospect of developing lanthanide organic phosphors for OLED applications.

In terms of OLED performance with high color purity in red emission, EL Eu^{3+} complexes present an unique opportunity as red-emitters for those striving for advanced technology solutions. In favor of inorganic Eu^{3+} emitters with comparable $^5D_0 \rightarrow {}^7F_J$ transition intensities ($J = 1$ and 2), Eu^{3+} complexes provide an asymmetrical ligand field that drastically facilitates the $^5D_0 \rightarrow {}^7F_2$ transition to yield an essentially monochromic single-band red emission at 612 nm (Fig. 1b). For common organic compounds, the generation of red emission typically requires a FMO energy gap of less than 2.0 eV, which is apparently too small for realizing energy level matching with adjacent charge transfer layers (CTLs). However, the matching of the energy levels with CTLs is feasible in Eu^{3+} complexes because their FMO energy gaps can be precisely controlled by ligand modification and functionalization. Owing to the highly localized emission nature of Eu^{3+}, moderate ligand conjugation and functionalization would not influence emission color purity of the resulting complex, thus allowing for convenient molecular design and integration of multiple functions. Since both singlet and triplet excitons can be harvested during EL processes, it is believed that the theoretical internal quantum efficiency of the devices made of Eu^{3+} complexes can approach to 100% [16].

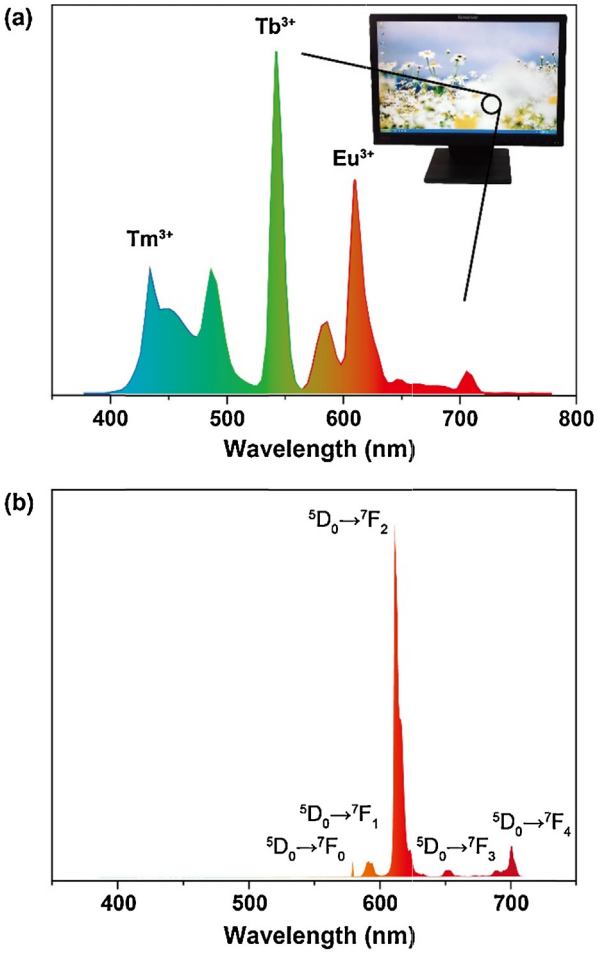

Fig. 1. (a) Emission spectrum of white-light area of Lenovo ThinkVision™ L197 display, recorded with a PR-655 Spectra Colorimeter at 150 cd m^{-2}; (b) typical photoluminescence spectrum of organic Eu^{3+} complexes.

In this article, the importance of Eu^{3+} complexes as EL materials for optoelectronic applications is reviewed. An overview describing