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Electronic Supporting Information Available

Efficient white polymer light-emitting diodes (WPLEDs) based on double emitting layers of PVK:Eu(III)-complex and Alq_3

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Supporting information

Materials and methods

High performance liquid chromatography (HPLC)-grade MeCN was purchased from Fisher Scientific and purified over solvent columns. Other solvents were used as received from Sigma Aldrich and stored over 3 Å activated molecule sieves. The typical H_2Salen (N,N'-bis(salicylidene)cyclohexane-1,2-diamine) Schiff-base ligand was synthesized from the condensation reaction[1] of an equimolar mixture of *cis*- and *trans*-1,2-diaminocyclohexane and salicylaldehyde from the literature. Other chemicals including materials PVK (Poly(*N*-vinylcarbazole); $M_w \approx 90000$ g/mol), Alq_3 and BCP et al for device fabrication, were commercial products of reagent grade and were used without further purification.

Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. Fourier Transform Infrared (FT-IR) spectra were recorded on a Nicolet Nagna-IR 550 spectrophotometer in the region 4000-400 cm^{-1} using KBr pellets. ^1H NMR spectra were recorded on a JEOL EX 400 spectrometer with $SiMe_4$ as internal standard in DMSO-d_6 at room temperature. ESI-MS was performed on a Finnigan LCQ^{DECA} XP HPLC-MS_n mass spectrometer with a mass to charge (*m/z*) range of 4000 using a standard electro-spray ion source and MeCN as the solvent. Electronic absorption spectra in the UV/Visible region were recorded with a Cary 300 UV spectrophotometer. Visible emission and excitation spectra were collected by a combined fluorescence lifetime and steady-state spectrometer (FLS-980, Edinburgh) with a 450 W Xe lamp. Excited-state decay times were obtained by the same spectrometer but with a μF900 Xe lamp. The luminescent absolute overall quantum yield (Φ_{em} *or* Φ_{Ln}^{L}) was determined by the same spectrometer using a 450 W Xe lamp and an integrating sphere. Thermal properties were characterized using thermogravimetric (TG) analyses on a NETZSCH TG 209 instrument under flowing nitrogen at a heating rate of 10 °C/min.

X-ray crystallography

X-ray quality crystals of complex [Zn(Salen)(μ-OAc)Tb(DBM)$_2$)] (**3**) were mounted onto thin glass fibers. Intensity data were collected on a Bruker SMART CCD diffractometer ((Mo-Kα radiation and λ = 0.71073 Å) in Φ and ω scan modes. Structures were solved by Direct methods followed by difference Fourier syntheses, and refined by full-matrix least-squares techniques against F^2 using SHELXTL.[2] All other non-hydrogen atoms were refined with anisotropic thermal parameters. Absorption corrections were applied using SADABS.[3] All hydrogen atoms were placed in calculated positions and refined isotropically using a riding model. Crystallographic data and selected bond lengths and angles are presented in Tables 1-2S, respectively. CCDC reference number 1561008 for complex **3**.

Cyclic voltammetry (CV) measurement

Cyclic voltammetry (CV) measurement was performed on a computer-controlled EG&G Potentiostat/Galvanostat model 283 at room temperature with a conventional three-electrode cell using using a an Ag/AgNO$_3$ (0.1 M) reference electrode, Pt carbon working electrode of 2 mm in diameter, and a platinum wire counter electrode. CV of the sample was performed in nitrogen-saturated dichloromethane containing 0.1 M Bu$_4$NPF$_6$ as supporting electrolyte. The cyclic voltammogram was measured at a scan rate of 100 mV·s^{-1}. The highest occupied molecular orbit (HOMO) and the lowest unoccupied molecular orbit (LUMO) energy levels of complex **3** are calculated according to the following equations,[4] $E_{\mathrm{HOMO}} = -(E_{\mathrm{OXD}} - E_{\mathrm{OXD,\ ferrocene}}) - 4.8$ eV, $E_{\mathrm{LUMO}} = E_{\mathrm{HOMO}} + E_{\mathrm{g}}$ eV, and where E_{g} is the energy band gap estimated from the low-energy edge of the absorption spectra from the samples. The HOMO and LUMO energy levels for the other used materials were obtained from the literature. [5]

PLEDs' fabrication and characterization

The **PLED-I** and **PLEDs-II-A-C** were fabricated on ITO coated glass substrates with a sheet of 20 Ω per square. Patterned ITO coated glass substrates were washed with acetone, detergent, distilled water and isopropanol in an ultrasonic bath. After being exposed under oxygen plasma for 20 min, PEDOT:PSS from water solution was spin-coated at 2000 rpm on the substrate and followed by drying in a vacuum oven at 140 °C for 20 min, giving a film of 40 nm. The chlorobenzene solution (at a concentration of 10 mg/mL) of PVK and a stipulated doping amount of complex **2** (20%, 30% or 40%; wt% *versus* PVK) as the EML1 was prepared under N_2 atmosphere and spin-coated on the PEDOT:PSS layer with a thickness of 40 nm. Subsequently, the Alq_3 layer (20 nm) as the EML2 and the following BCP layer (20 or 10 nm) were thermally deposited onto the EML1. Finally, a thin layer of LiF (1 nm) followed by 100 nm thickness Al capping layer was deposited onto the substrate under vacuum of 5×10^{-6} Pa. The typical active area of the four devices is 9 mm^2. Current density (J)-voltage (V)-luminance (L) was collected using a Keithley 2400 source meter equipped with a calibrated silicon photodiode. The electroluminescent spectra were measured by a PR655 spectrometer. The eternal quantum efficiency (η_{EQE}) values were determined by a Si photodiode with calibration in an integration sphere (IS080, Labsphere).

References

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Table 1S Crystallographic data and structure refinement for complex **3**.

compound	**3**
formula	$C_{52}H_{45}N_2O_8ZnTb$
fw	1050.19
cryst syst	Monoclinic
space group	*P2(1)/n*
a, Å	14.288(5)
b, Å	13.854(5)
c, Å	28.391(10)
α, deg	90
β, deg	103.983(9)
γ, deg	90
V, Å^3	5453(3)
Z	4
ρ, g·cm^{-3}	1.279
size, mm	0.22 × 0.21 × 0.19
μ(Mo-Kα), mm^{-1}	1.774
data/restraints/parameters	9611/725/577
quality-of-fit indicator	0.891
final R indices [$I > 2\sigma(I)$]	R_1 = 0.111
	wR_2 = 0.2437
R indices (all data)	R_1 = 0.3187
	wR_2 = 0.3314

Table 2S Selected bond lengths (Å) and bond angles (°) in complex **3**.

3			
Zn(1)-N(1)	2.060(20)	Zn(1)-N(2)	2.030(20)
Zn(1)-O(1)	2.020(16)	Zn(1)-O(2)	2.034(14)
Zn(1)-O(7)	1.994(17)		
Tb(1)-O(1)	2.318(14)	Tb(1)-O(2)	2.256(15)
Tb(1)-O(3)	2.201(16)	Tb(1)-O(4)	2.237(15)
Tb(1)-O(5)	2.228(15)	Tb(1)-O(6)	2.243(14)
Tb(1)-O(8)	2.317(16)	Zn(1)···Tb(1)	3.277(3)
N(1)-Zn(1)-N(2)	80.8(10)	N(1)-Zn(1)-O(1)	88.8(9)
N(1)-Zn(1)-O(2)	151.9(8)	N(1)-Zn(1)-O(7)	110.6(8)
O(1)-Tb(1)-O(2)	72.6(5)	O(1)-Tb(1)-O(8)	75.5(5)
O(3)-Tb(1)-O(4)	75.9(6)	O(5)-Tb(1)-O(6)	73.4(5)

Scheme 1S. Synthesis scheme of the complex precursor [Zn(Salen)(MeCN)] and its complexes **1**-**4**.

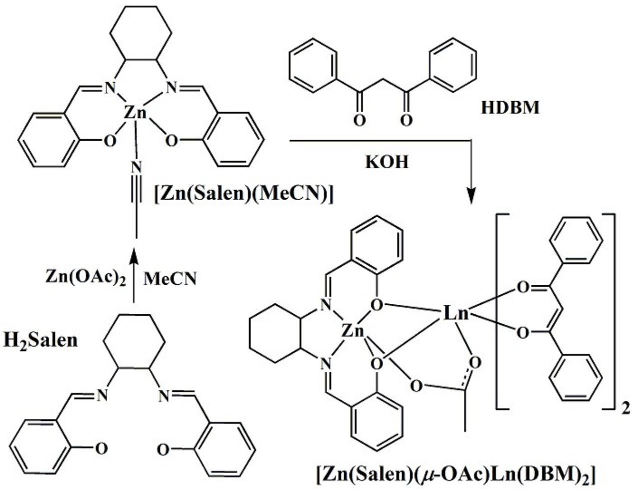

Figure 1S. TGA curves of complex **2** and PVK.

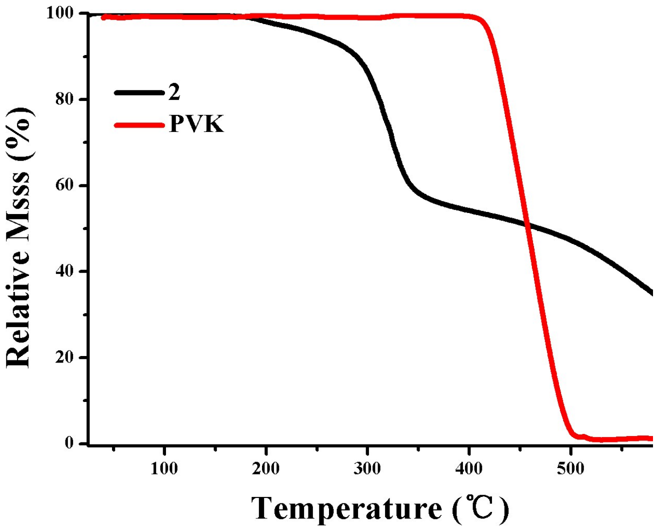

Figure 2S. Normalized UV-visible absorption spectra of the free ligand HDBM, the complex precursor [Zn(Salen)(MeCN)] and their complexes **2**-**4** in MeCN solution (10^{-5} M) and photo-luminescent spectrum of PVK in film.

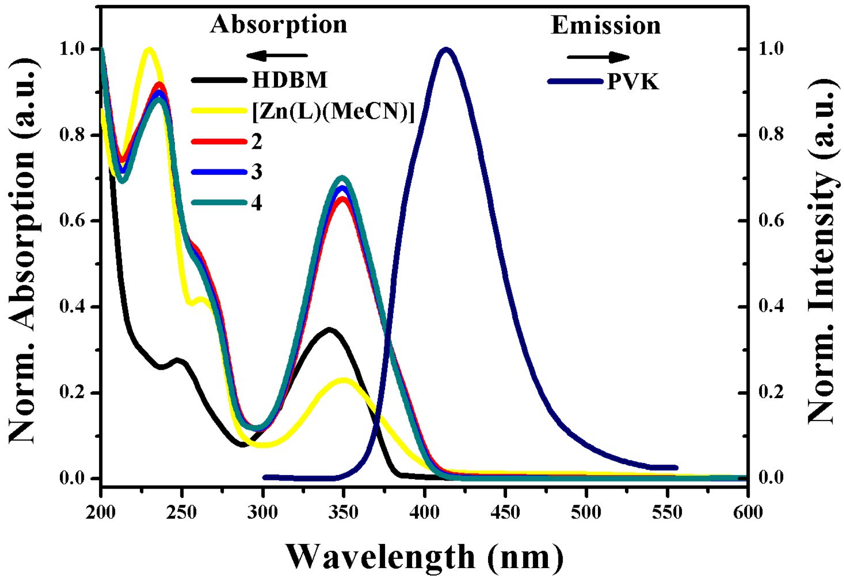

Figure 3S. Schematic energy level diagram and possible energy transfer for the complexes **2**-**3** and the EML1 of PVK:complex **2**.

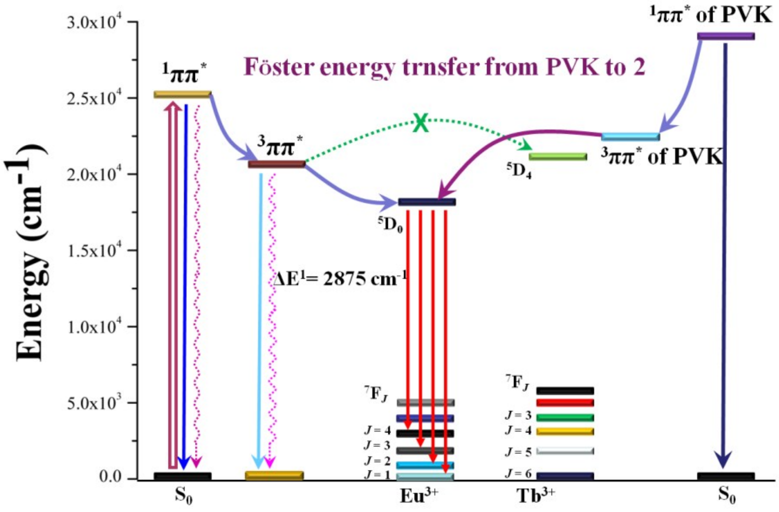

Figure 4S. Normalized visible emission spectra of PVK:complex **2** (20, 30 or 40 wt% of the doping content of complex **2** in PVK) in the solid state at RT.