Ternary complex [Sm(acac) (5-Br-2,2'-bpy)] for the solution-processed white polymer light-emitting diode (WPLED)

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ARTICLE INFO

Keywords:

Tris- β -diketonate-Sm³⁺-complex
Dichromatic integration
Direct white-light
White polymer light-emitting diode

ABSTRACT

In consideration of the Sm³⁺-centered characteristic orange-light as the ideal color-primary component toward a dichromatic white-light, herein, through the doping of the complex [Sm(acac)₃(5-Br-2,2'-bpy)] (**2**; Hacac $\frac{1}{4}$ acetylacetone; 5-Br-2,2'-bpy $\frac{1}{4}$ 5-Br-2,2'-bipyridine) into the PVK (PVK $\frac{1}{4}$ poly(N-vinyl-carbazole)) host, the obtained **PVK@2** film (10:1, wt/wt) exhibits the straightforward solid-state white-light (Φ_{PL} $\frac{1}{4}$ 6.7%). Further using the **PVK@2** film (10:1; wt/wt) as the emitting layer, its single-component solution-processed WPLED gives the electroluminescent performance (L^{Max} of 360.9 cd/m², η^{Max} of 1.08 cd/A) satisfactory enough for portable full-color flat displays.

1. Introduction

Contributing from the receptive “antenna” effect [1], the Sm³⁺-centered orange-light ($^4G_{5/2} \rightarrow ^6H_{5/2}$; $J \frac{1}{4}$ 5, 7, 9 or 11) [2] can be sensitized through the Laporte- and spin-allowed ligand-centered transition ($^0S \rightarrow ^1S$) followed by the inter-system crossing (ISC; $^1S \rightarrow ^1T$) and the $^1T \rightarrow \text{Sm}^{3+}$ energy transfer for one certain organo-Sm³⁺ complex. Especially toward the high efficiency [3] of its Sm³⁺-centered high-purity orange-light, the selection of a suitable organic ligand is of paramount importance, from which, the strong absorption, the maximized energy transfer and the minimized radiationless deactivation should be simultaneously ensured [4]. Till now, compared with the concerted efforts to vacuum-deposited [5] or solution-processed [6] orange-light organic/polymer light-emitting diodes (OLEDs/PLEDs), the realization of reliable WOLEDs/WPLEDs using organo-Sm³⁺ complex as the emitter lags far behind [7], despite the theoretically dichromatic, trichromatic or tetrachromatic white-light production [8] smoothly incorporated with the Sm³⁺-centered color-primary orange-light.

As a matter of fact, among organo-Sm³⁺ hybrid materials, although Sm³⁺-relative metal-organic frameworks (MOFs) or coordination polymers [9], are prevalent white-light-emitting solid-state materials promising for white LEDs (WLEDs) [10], the inherent deficiency of their processing (vacuum-deposition or solution-process) inability, limits the utilization in WOLEDs/WPLEDs. By contrast, available of the necessary film-formation for sublimable small-molecule organo-Sm³⁺ complexes or organo-Sm³⁺-incorporated polymers,

their WOLEDs/WPLEDs with the Sm³⁺-centered orange-light as the color-primary component could theoretically be expectable. From the perspective of the targeted electric-driven white-light, one feasible approach can rely on the insufficient color-primary component of the organo-Sm³⁺ complex, where its WOLEDs/WPLEDs generation, should be strictly dependent on the organo-Sm³⁺-included multi-component emitters or multiple-layering fabrication. As an alternative one, based on the single-component organo-Sm³⁺-emitter with the straightforward white-light, the realization of its WOLEDs/WPLEDs could be superior, owing to the significantly simplified structure without additional color supplementation. Herein, in light of the pioneered dichromatic WOLED [7] fabricated with NPB-[Sm(DBM)₃(phen)] (NPB $\frac{1}{4}$ *N,N'*-di(naphthalen-1-yl)-*N,N'*-diphenyl-[1,1'-biphenyl]-4,4'-diamine, DBM $\frac{1}{4}$ dibenzoylmethane; phen $\frac{1}{4}$ 1,10-phenanthroline) co-deposited emitters, its stable and voltage-independent electroluminescent white-lights (CIE chromatic coordinates $x \frac{1}{4}$ 0.32–0.28, $y \frac{1}{4}$ 0.28–0.33), responsible from the single-component NPB-[Sm(DBM)₃(phen)] exciplex, are considerably attractive. Nonetheless, besides the vacuum-deposition high-cost, the WOLED still suffers from unsatisfactory electroluminescent performance (η^{max} $\frac{1}{4}$ 0.17 cd/A), which significantly inferior to the parameter for solid-state lighting [11], is even unsatisfactory enough to that ($\eta_c > 0.5$ cd/A) fundamentally required for low-cost portable full-color flat displays [12]. To circumvent the two issues above, herein, we envision a conceptual strategy of doping with specific organo-Sm³⁺ complex and one suitable polymer to their solution-processed WPLEDs. On one hand, considering the efficient orange-light of [Sm(acac)₃(5-Br-2,2'-bpy)] (**2**; Scheme

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** Corresponding author. Both authors contributed equally to the study. <https://doi.org/10.1016/j.optmat.2020.109936>

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Received 15 January 2020; Received in revised form 11 March 2020; Accepted 20 April 2020 Available online 11 June 2020
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1) and the excellent rheological property of blue-light-emitting PVK, the doping **PVK@2** systems should endow an capability of directly dichromatic white-light for structure-simplified and solution-processable WPLEDs. On the other hand, the additional Forster ϵ energy transfer [13] from the PVK host to the guest ([Sm(acac)₃(5-Br-2,2'-bpy)] (**2**)) can be further motivated within the single-component **PVK@2** systems, which, together with the balance of electron-transport and PVK-assisted hole-transport, probably give the improved electroluminescence of their cost-effective WPLEDs satisfactory enough for portable full-color flat displays [12].

2. Experimental

The information of starting materials and characterization methods was shown in the detailed Electronic Supporting Information (ESI). The ancillary ligand **5-Br-2,2'-bpy** was obtained from the Stille coupling reaction [14] between 2,5-dibromopyridine and 2-(tributylstannyl) pyridine in the presence of Pd(PPh₃)₄ (0). As to the series of dihydrate Ln³⁺-complex precursors [Ln(acac)₃(H₂O)₂] (Ln $\frac{1}{4}$ La, Sm or Gd), they were synthesized according the well-established procedure from the literature [15].

2.1. Synthesis of the ternary tris- β -diketonate-Ln³⁺ complexes [Ln(acac)₃(5-Br-2,2'-bpy)] (Ln $\frac{1}{4}$ La (**1**); Ln $\frac{1}{4}$ Sm (**2**) or Ln $\frac{1}{4}$ Gd (**3**))

To a MeOH solution (10 mL) of the Ln³⁺-complex precursor [Ln(acac)₃(H₂O)₂] (0.2 mmol; Ln $\frac{1}{4}$ La, Sm or Gd), another MeOH solution (10 mL) containing **5-Br-2,2'-bpy** (0.2 mmol, 0.047 g) was added, and the resulting mixture was refluxed under a N₂ atmosphere for another 3 h. After cooling to room temperature, each of the obtained clear solutions was filtered, and left to stand for several days to afford the microcrystalline products **1–3**, respectively. For [La(acac)₃(5-Br-2,2'-bpy)] (**1**): Yield: 0.046 g, 69%. Anal. Calcd for C₂₅H₂₈N₂O₆BrLa: C, 44.73; H, 4.20; N, 4.17%. Found: C, 44.79; H, 4.15; N, 4.21%. FT-IR (KBr, cm⁻¹): 3005 (w), 2359 (w), 2344 (w), 1587 (m), 1516 (s), 1449 (m), 1373 (vs), 1364 (s), 1275 (m), 1260 (m), 1140 (w), 1121 (w), 1084 (w), 1061 (w), 1038 (w), 1016 (w), 1001 (m), 935 (w), 916 (w), 841 (w), 785 (m), 764 (s), 748 (s), 669 (m), 631 (m), 530 (w). ¹H NMR (400 MHz, DMSO-*d*₆): δ

Scheme 1. The synthetic scheme of the ancillary ligand **5-Br-2,2'-bpy** and its ternary tris- β -diketonate-Ln³⁺ complexes [Ln(acac)₃(5-Br-2,2'-bpy)] (Ln $\frac{1}{4}$ La (**1**); Sm (**2**) or Gd (**3**)).

(ppm) 8.82 (d, 1H, -Py), 8.70 (d, 1H, -Py), 8.35 (t, 2H, -Py), 8.20 (q, 1H, -Py), 7.97 (t, 1H, -Py), 7.49 (q, 1H, -Py), 5.19 (s, 3H, -CH₃), 1.73 (s, 18H, -CH₃). ESI-MS (in CH₃CN) m/z : 670.02 (100%), [M - H]⁺.

For [Sm(acac)₃(5-Br-2,2'-bpy)] (**2**): Yield: 0.051 g, 75%. Anal. Calcd for C₂₅H₂₈N₂O₆BrSm: C, 43.98; H, 4.13; N, 4.10%. Found: C, 43.91; H, 4.18; N, 4.14%. FT-IR (KBr, cm⁻¹): 2992 (w), 2359 (w), 2342 (w), 1584 (m), 1514 (s), 1456 (m),

1377 (vs), 1256 (m), 1188 (w), 1015 (m), 955 (w), 916 (m), 851 (w), 754 (m), 671 (m), 608 (w), 530 (w). ESI-MS (in CH₃CN) m/z : 683.03 (100%), [M - H]⁺.

For [Gd(acac)₃(5-Br-2,2'-bpy)] (**3**): Yield: 0.054 g, 78%. Anal. Calcd for C₂₅H₂₈N₂O₆BrGd: C, 43.54; H, 4.09; N, 4.06%. Found: C, 43.59; H, 4.15; N, 4.01%. FT-IR (KBr, cm⁻¹): 3005 (w), 2359 (w), 2342 (w), 1584 (s), 1514 (s), 1456 (m), 1435 (m), 1387 (vs), 1362 (m), 1312 (w), 1260 (s), 1138 (w), 1115 (w), 1092 (w), 1045 (w), 1015 (m), 920 (m), 851 (w), 791 (m), 764 (s), 750 (s), 733 (w), 648 (w), 528 (w). ESI-MS (in CH₃CN) m/z : 691.04 (100%), [M - H]⁺.

2.2. Synthesis of the **PVK@2** film-typed hybrid materials doped with the complex **2** into the PVK host with different mass ratios

To a toluene solution (30 mL) containing the commercial PVK (M_w: 90000 g/mol; PDI $\frac{1}{4}$ M_w/M_n: 1.5), the complex **2** at a stipulated mass ratio (10:1, 10:3 or 10:5; wt/wt) relative to the PVK was added, and the resultant mixture was continuously stirred at room temperature overnight. After removal of the solvent and cooling to room temperature, the mixture was spin-coated at 3000 rpm on a clean quartz slide, and then dried in air. The almost similar film thickness of 90 nm was measured by ellipsometry through collecting data every 5 from 65 to 75 and fitted using a Cauchy film on a gold model. For the **PVK@2** films: Yield: 96% (10:1; wt/wt); 98% (10:3; wt/wt) or 99% (10:5; wt/wt). Representative FT-IR (KBr, cm⁻¹): 2956 (w), 2362 (w), 1638 (w), 1610 (s), 1594 (s), 1582 (s), 1536 (w), 1490 (s), 1438 (m), 1396 (w), 1368 (m), 1314 (w), 1275 (w), 1229 (w), 1074 (m), 1022 (w), 1003 (m), 908 (w), 841 (w), 810 (w), 789 (w), 753 (vs), 692 (m), 650 (m), 631 (w), 598 (w), 511 (w).

2.3. WPLEDs' fabrication and characterization

Using the synthesized **PVK@2** film (10:1, wt/wt) with the straightforward solid-state white-light as the single-component emitting layer, its WPLED was fabricated through a typically solution-processed procedure, configuring with ITO/PEDOT:PSS (40 nm)/**PVK@2** (90 nm)/BCP (10 nm)/TPBi (30 nm)/LiF (1 nm)/Al (100 nm). Among these materials, ITO (indium tin oxide) was the coated glass substrate, and PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)) was used as the hole-injecting material. BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) acts as the hole-blocking layer, and TPBi (1, 3, 5-*tris*(2-*N*-phenylbenzimidazolyl))

functions to facilitate the electron-transporting ability in the WPLED. The details of the WPLED's fabrication and testing are depicted in the Electronic Supporting Information.

3. Results and discussion

3.1. Synthesis, characterization and photo-physical property of the ternary tris- β -diketonate-Ln³⁺ complexes **1–3**

Through the Stille coupling reaction [14] between 2,5-dibromopyridine and 2-(tributylstannyl)pyridine in the presence of $\text{Pd}(\text{PPh}_3)_4$ (0), the ancillary ligand **5-Br-2,2'-bpy** was obtained in the yield of 67%. Further based on the reaction of equimolar amount of the Ln^{3+} -complex precursor $[\text{Ln}(\text{acac})_3(\text{H}_2\text{O})_2]$ ($\text{Ln} \propto \text{La, Sm or Gd}$) [15] and the ancillary ligand **5-Br-2,2'-bpy**, also as shown in Scheme 1, the series of ternary *tris*- β -diketonate- Ln^{3+} complexes **1–3** were obtained in 69–78% yields, respectively.

The complexes **1–3**, soluble in common organic solvents, were well characterized by EA, FT-IR, ^1H NMR and ESI-MS. In the ^1H NMR spectrum of the *anti*-ferromagnetic $[\text{La}(\text{acac})_3(5\text{-Br-2,2'}\text{-bpy})]$ (**1**), besides the combined proton resonances ($\delta \propto 8.82\text{--}1.73$ ppm) of both the deprotonated ligand (**acac**[−]) and the ancillary ligand **5-Br-2,2'-bpy** in a stipulated molar ratio of 3:1, the enolic $\text{--CH}^-\text{C}$ proton signal ($\delta \propto 5.19$ ppm) of the (**acac**[−]) ligand should be resulted from the La^{3+} -coordination. Moreover, the ESI-MS spectra of the complexes **1–3** exhibit a strong mass peak at m/z 672.02 for $[\text{La}(\text{acac})_3(5\text{-Br-2,2'}\text{-bpy})]$ (**1**), 683.03 for $[\text{Sm}(\text{acac})_3(5\text{-Br-2,2'}\text{-bpy})]$ (**2**) or 691.04 for $[\text{Gd}(\text{acac})_3(5\text{-Br-2,2'}\text{-bpy})]$ (**3**) assigned to the major species $[\text{M} \text{H}]^+$, respectively. These observed results confirm that every ternary *tris*- β -diketonate- Ln^{3+} species of the complexes **1–3** can be retained in the respective solution.

The electronic absorption spectra of the two free ligands **Hacac** and **5-Br-2,2'-bpy** and their ternary *tris*- β -diketonate- Ln^{3+} complex **2–3** were recorded in dilute MeCN solutions as shown in Fig. 1. Owing to the Ln^{3+} -coordination, the complex **2–3** display the similar ligands-based while significantly broadened (200–410 nm) absorptions ($\lambda_{\text{ab}} \propto 247\text{--}248$ and $284\text{--}287$ nm) relative to those (<350 nm) of the two (**Hacac** and **5-Br-2,2'-bpy**) free ligands. The molar absorption coefficients of the complexes **2–3** in the lower energy (284–287 nm) $\pi\text{--}\pi^*$ -transitioned absorption bands are almost three orders of magnitude larger than those of the two (**Hacac** and **5-Br-2,2'-bpy**) free ligands, which should be due to their ternary *tris*- β -diketonate- Ln^{3+} component with the enhanced π -conjugation effect. For the Sm^{3+} -based complex **2**, up photo-excitation of the chromophores at the range of 200–410 nm ($\lambda_{\text{ex}} \propto 340$ nm), as shown in Fig. 2, the strong Sm^{3+} -centered characteristic emissions (568 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ transition), 607 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ transition), 652 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ transition) and 712 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{11/2}$ transition)) and the weak while detectable emission peaking at $\lambda_{\text{em}} \propto 394$ nm are concurrently observed. Moreover, besides the *hyper*-sensitive $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ electronic-dipole transition at 652 nm, the intensity ratio between it and the $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ magnetic-dipole transition (568 nm) is up to 4.9, implying that the central Sm^{3+} ion of the complex $[\text{Sm}(\text{acac})_3(5\text{-Br-2,2'}\text{-bpy})]$ (**2**) is located in a site without inversion symmetry [16]. And thus, the complex **2** emits a bright orange-light with the CIE (Commission International De L'Eclairage) chromatic

Fig. 1. The UV–visible absorption spectra of the β -diketonate-typed ligand **Hacac**, the ancillary ligand **5-Br-2,2'-bpy** and their ternary *tris*- β -diketonate- Ln^{3+} complexes **2–3** and the emission of PVK in dilute MeCN solution at room temperature.

Fig. 2. The excitation and visible emission spectra of complexes $[\text{Sm}(\text{acac})_3(5\text{-Br-2,2'}\text{-bpy})]$ (**2**) and $[\text{Gd}(\text{acac})_3(5\text{-Br-2,2'}\text{-bpy})]$ (**3**) in dilute MeCN solution (1×10^{-5} M) at room temperature or 77 K.

coordinate $x \propto 0.567$ and $y \propto 0.349$.

As a reference compound, the Gd^{3+} -based complex **3** allows the further exploration of the antennae luminescence in the absence of energy transfer, because the Gd^{3+} ion has no energy levels below 32000 cm^{-1} , and therefore cannot accept any energy from the antennae excited state [17]. For the Gd^{3+} -centered complex **3** in solution at room temperature, it shows the typically ligands-based fluorescence ($\lambda_{\text{em}} \propto 394$ nm and $\tau \propto 1.02$ ns) also shown in Fig. 2. By contrast, the Gd^{3+} -centered complex **3** displays the 0-0 transition phosphorescence ($\lambda_{\text{em}} \propto 433$ nm and $\tau \propto 0.98 \mu\text{s}$) at 77 K, from which, the triplet ($^3\pi\text{--}\pi^*$) energy level of 23095 cm^{-1} is obtained. With regard to the singlet ($^1\pi\text{--}\pi^*$) energy level (27855 cm^{-1}) estimated from the lower wavelength (359 nm) of its UV–visible absorbance edge, the energy gap ΔE^1 ($^1\pi\text{--}\pi^* - ^3\pi\text{--}\pi^*$, 4760 cm^{-1} ; Fig. 1S) near to the desirable 5000 cm^{-1} , endows a relatively effective ISC process according to the Reinholdt's empirical rule [18]. Meanwhile, ruled by the Latva's empirical rule [19], the second energy gap ΔE^2 (5171 cm^{-1} ; $^3\pi\text{--}\pi^* - ^4\text{G}_{5/2}$) between the ligands-based $^3\pi\text{--}\pi^*$ energy and the first excited state $^4\text{G}_{5/2}$ (17924 cm^{-1}) of Sm^{3+} ion is large enough to sensitize the Sm^{3+} -centered orange-light. Therefore, the radiative transition of the $^1\pi\text{--}\pi^*$ energy, together with the following effective $^3\pi\text{--}\pi^* \rightarrow ^4\text{G}_{5/2}$ transition of Sm^{3+} ion, should be the reason to the dual emissions for the Sm^{3+} -based complex **2**. Further based on the lifetime-decayed experiments of the Sm^{3+} -based complex **2**, the $\tau \propto 0.84$ ns at $\lambda_{\text{em}} \propto 394$ nm) for the weak ligands-based fluorescence and the $\tau \propto 64 \mu\text{s}$ at $\lambda_{\text{em}} \propto 651$ nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ transition) for the Sm^{3+} -centered strong phosphorescence also verify its dual-emissive nature. Worthy of notice, the absolute quantum efficiency ($\Phi_{\text{sm}}^{\text{abs}}$) of the complex **2** characteristic of the Sm^{3+} -centered orange-light is up to 5.8%, which is at the top level among previously reported organo- Sm^{3+} -complexes [5,6] for orange-light OLEDs.

3.2. Color-tunable emissions included direct white-light of the PVK@2 film-typed hybrid materials with different mass ratios

To realize the straightforward dichromatic white-light, the series of single-component doping-typed hybrid materials **PVK@2** with different mass ratios (10:1, 10:3 and 10:5; wt/wt) were obtained. In both of the FT-IR and PXRD (Fig. 2S) characterizations, the **PVK@2** films exhibit the almost PVK-characteristic

nature, which should be arisen from the low-concentration disperse of the complex **2** into the polymeric PVK. Moreover, for the representative **PVK@2** film (10:1; wt/wt), its TG analysis result (Fig. 3S) shows the significantly improved decomposition temperature (T_d % 389 C at 5% weight loss) in comparison to that (272 C) of the complex **2**. Especially, the determined T_g (glass transformation temperature) of 195 C renders the **PVK@2** film (10:1; wt/wt) a particular opportunity to its solution-processable WPLEDs.

Owing to the significant overlap (also Fig. 1) between the emission of the PVK host and the absorption of the complex **2** within the 280–310 nm range, effective Forster energy transfer [€ 13] from the PVK host to the complex **2** should be motivated for the **PVK@2** films. This range (λ_{ex} % 280–310 nm) with every 10 nm step-size can be used the suitable excitation regime to realize the concurrent emissions of both the PVK-based blue-light and the orange-light of the complex **2** for the dichromatic-modulated white-light. Toward it, upon λ_{ex} % 280–310 nm, the photo-luminescent properties of the **PVK@2** films with different mass ratios (10:1, 10:3 and 10:5; wt/wt) were examined at room temperature, and summarized in Figs. 3–4. For the **PVK@2** film (10:1; wt/wt), photo-excitation at the range of 280–310 nm, as shown in Fig. 3, gives rise to two-centered while broad-ranging emissions of 400–750 nm assigned to the PVK-based blue-light (422 nm) and the Sm^{3+} -centered ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{J/2}$ transitions; J % 5, 7, 9 and 11) orange-light, respectively. Moreover, the two-centered relative intensity is strictly dependent on the excitation wavelength, where with the increase of the excitation wavelength, the orange-to-blue relative intensity ratio increases, correspondingly, indicating that effective Forster energy transfer [€ 13] from the PVK host to the complex **2** actually takes place. As expectable, the combination of the two-centered emissions leads to all the resultant colors (Points I-A-D; x % 0.255–0.277, y % 0.196–0.198) falling well within the white-light region. The CCTs of 1759–1917 K and the CRIs within 78–79, render the dichromatic-integrated colors characteristic of warm-white-lights. Interestingly, the warm-white-lights are highly stable with little color-coordinate shifts ($|\Delta x| < 0.03$, $|\Delta y| < 0.01$), which should be resulted from the Sm^{3+} -centered orange-light-primary resource for the **PVK@2** film (10:1; wt/wt). In particularly, excitation of 310 nm is found to produce the best

white-light (Point I-D; x % 0.277, y % 0.196, CCT of 1891 K and CRI of 79), whose quantum yield up to 6.7% is at the top level within previously reported organo- Sm^{3+} -doping systems [5,6] for orange-light OLEDs/PLEDs. Meanwhile, the 32 ns lifetime of PVK-incorporated blue-light (λ_{em} % 422 nm) and the Sm^{3+} -decayed (λ_{em} % 651 nm) lifetime of 216 μs , confirm that the optimal white-light (Point I-D) should unambiguously originate from the both fluorescence and phosphorescence dichromatic-incorporation.

Increasing the Sm^{3+} -doping content up to 10:3 (wt/wt), also leads to the two-centered emissions shown in Fig. 4(a), while the domination of the Sm^{3+} -centered orange-light within, should be arisen from the relatively higher Sm^{3+} -doping content (10:3; wt/wt). Therefore, in contrast to the direct warm-white-lights (Fig. 3) for the **PVK@2** film (10:1; wt/wt), all the integrated colors upon λ_{ex} % 280–310 nm are beyond the white-light regime, exhibiting the purplish-pink lights (Points II-A-D; x % 0.371–0.443, y % 0.243–0.275). However, the pronounced Sm^{3+} -centered orange-lights render the λ_{ex} -regulated purplish-pink-emitting coordinates a relatively large shifts in the $|\Delta x| < 0.8$ and $|\Delta y| < 0.4$ ranges. Further increasing the doping content of the Sm^{3+} -based complex **2** for the **PVK@2** film (10:5; wt/wt), the dichromatic integration of both the dominated Sm^{3+} -centered orange-light and the blue-light from the organic moiety (including PVK and the ligands-based residual) gives rise to the λ_{ex} -regulated pink light (Fig. 4(b); Points III-A-D; x % 0.460–0.521, y % 0.292–0.316). Worthy of notice, the blue-light species of the **PVK@2** films with different doping contents (10:1; 10:3 and 10:5; wt/wt), decay with an almost constant lifetime (32–34 ns), which should be arisen from the saturated color-compensation [13] of the PVK host. By contrast, besides the non-multiple population of the $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{J/2}$ transition hyper-sensitive intensity, the Sm^{3+} -decayed (λ_{em} % 651 nm) phosphorescent lifetime (τ % 184 μs) for the **PVK@2** film (10:5; wt/wt) is relatively shorter than those (τ % 212–216 μs) with the lower doping concentrations, indicative of an occurrence of aggregation-induced quenching [3] with the 10:5 doping content.

3.3. Electroluminescent performance of the single-component WPLED based on the **PVK@2** film (10:1; wt/wt)

To further elucidate the suitability of the PVK host for doping of the complex **2**, the electrochemical property of the orange-light complex **2** in anhydrous MeCN solution was investigated and the HOMO and LUMO energy levels were calculated. In the cyclic voltammogram shown in Fig. 4S, an oxidation potential of 1.21 V versus Fc^+/ Fc is detected, from which, the HOMO level of the complex **2** is estimated to be 5.47 eV. Despite no distinctive

Fig. 4. The λ_{ex} -dependent emission spectra and corresponding CIE chromatic coordinates (inset) of the solid-state **PVK@2** film with different mass ratios (10:3 (4a))

Fig. 3. The λ_{ex} -dependent color-tuning white-light emissions and corresponding CIE chromatic coordinates (inset) of the solid-state **PVK@2** film with (10:1; wt/wt) at room temperature. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

reduction wave for the complex **2**, a reasonable E_{OPT} of 3.45 eV estimated from its absorbance edge (359 nm, also Fig. 1) gives the LUMO level of 2.02 eV. Both the HOMO and LUMO energy levels of the complex **2** fall within those (5.50 and 2.00 eV) of the PVK with shallow trap depths (0.02–0.03 eV). This shows that the blue-light-emitting PVK characteristic of excellent hole-transport is an ideal host for the doped complex **2**.

On the other hand, in consideration of the inherently higher mobility ($10^3 \text{ cm}^2/\text{V}\cdot\text{s}$) of holes than that ($10^3 \text{ cm}^2/\text{V}\cdot\text{s}$) of electrons, the electron-transporting TPBi layer and the BCP layer functioning as the hole-blocking layer, are concurrently utilized to improve the carrier recombination. Therefore, based on the **PVK@2** film (10:1; wt/wt) with

Fig. 5. a) The device structure with the energy level diagram; b) The normalized electroluminescent spectra with CIE coordinates inserted; c) The L - V and J - V curves; d) The $\eta_{\text{EQE}}-L$, $\eta_{\text{P}}-L$ and $\eta_{\text{C}}-L$ curves for the WPLED based on the PVK@2 film (10:1; wt/wt). and 10:5 (4b); wt/wt) at room temperature.

the direct solid-state white-lights as the emitting layer, its single-component solution-processed WPLED was fabricated, and the electroluminescent performance was summarized in Fig. 5. According to the proposed energy level diagram for the WPLED shown in Fig. 5(a), the two HOMO levels (5.50~5.47 eV) of PVK and the complex **2** are well between those (6.20~5.20 eV) of TPBi and PEDOT:PSS, and thus, the injected electrons and holes could be trapped and recombined within the white-light-emitting species **PVK@2** (10:1, wt/wt). As expected and shown in Fig. 5(b), the normalized electroluminescent spectra of the WPLED actually exhibit the simultaneous emissions of the PVK-based blue-light (λ_{em} 422 nm) and the Sm^{3+} -centered (λ_{em} 651 nm) orange-light throughout the whole applied bias voltage range (6.0–18.0 V). Meanwhile, their dichromatic integration gives rise to the electric-driven white-light. However, in contrast to the doping concentration and λ_{ex} -relative white-light production for the photo-luminescent **PVK@2** film (10:1; wt/wt), its electroluminescent white-lights are highly dependent on the applied bias voltages. Owing to the carrier-trapping mechanism during the electric-driven process, after the turn-on voltage (V_{on} at 1 cd/m^2) of 8.5 V, the integrated white-lights (CIE chromatic coordinates x 0.257–0.287, y 0.192–0.216) are highly stable within the applied bias voltages of 8.5–12 V, and then the higher applied bias voltages (12.5–18 V) render the white-lights' chromatic coordinates waving within a broadened range (CIE chromatic coordinates x 0.299–0.363, y 0.251–0.366). Despite the best white-light (CIE chromatic coordinate x 0.335, y 0.303, CCT of 5313 K and CRI of 84) occurring at 14 V, it characteristic of a significantly increased orange-to-blue relative intensity ratio, should be the imbalanced carrier-transport with doping-induced phase-separation. As shown in Fig. 5(c), with the voltage increasing from 8.5 V to 12.5 V, both the luminance (L , cd/m^2) and the current density (J , mA/cm^2) monotonously increase, and the L^{Max} of 360.9 cd/m^2 is achieved at 12.5 V with a current density of 1136 mA/cm^2 . Moreover, during that increase of the applied bias voltage or the luminance, as shown in Fig. 5(d), all the efficiencies (η_{e} , η_{p} , and η_{EQE}) increase first and insistently decrease with the $\eta_{\text{e}}^{\text{Max}}$ of 1.08 cd/A , the $\eta_{\text{p}}^{\text{Max}}$ of 0.36 lm/W and the $\eta_{\text{EQE}}^{\text{Max}}$ of 1.05% at 9.5 V (L 15 cd/m^2), respectively. Upon the applied bias voltage up to 12.5 V, the heavy (ca. 75%) efficiency-roll-offs of the WPLED are observed, which should mainly be attributed to Sm^{3+} -centered phosphorescence lifetime being too long [6a]. Nonetheless, the single-component WPLED's performance (the $\eta_{\text{e}}^{\text{Max}}$ of 1.08 cd/A , the $\eta_{\text{p}}^{\text{Max}}$ of 0.36 lm/W and the $\eta_{\text{EQE}}^{\text{Max}}$ of 1.05%) is record-renewed to those of previously organo- Sm^{3+} -based WOLEDs [7], and satisfactory enough to the requirements for portable full-color flat displays [12]. Further increasing the applied bias voltage (>12.5 V), its significantly inferior performance should be attributed to the aging of the WPLED.

4. Conclusions

In summary, based on the efficient orange-light of the complex [Sm(acac)₃(5-Br-2,2'-bpy)] (**2**) and the blue-light of PVK as the color-primary components, the doping-typed **PVK@2** films exhibit the doping concentration and λ_{ex} -relative dichromatic color-tuning (white-light to purplish-pink and to pink). Further using the **PVK@2** film (10:1; wt/wt) with the straightforward white-light (Φ_{PL} 6.7%) as the emitting layer, its single-component solution-processed WPLED exhibits the electroluminescent performance (L^{Max} of 360.9 cd/m^2 , $\eta_{\text{e}}^{\text{Max}}$ of 1.08 cd/A) satisfactory enough for portable full-color flat displays.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work is funded by the National Natural Science Foundation (21373160, 21173165), the MOE Laboratory of Bioinorganic and Synthetic Chemistry, the

State Key Laboratory of Structural Chemistry (2019), the Postdoctoral Science Foundation (2018M633564), the Fundamental Research Fund for the Central Universities (G2018KY0308), the Graduate Innovation and Creativity Fund (YZZ17127) of Northwest University in China.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.optmat.2020.109936>.

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