Single-component white polymer light-emitting diode (WPLED) based on a binary *tris*-pyrazolonate-Sm-complex

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ABSTRACT

Based on the doping of the binary *tris*-pyrazolonate-Sm³⁺ complex [Sm(tba-PMP)₃(5-Br-2,2'-bpy)] (1; 5-Br-2,2'-bpy % 5-bromo-2,2'-bipyridine and Htba-PMP % 1-phenyl-3-methyl-4-(*tert*-butylacetyl)-5-pyrazolone) with an efficient orange-light into the PVK (poly(*N*-vinylcarbazole) host, the obtained **PVK@1** films exhibit the dichromatic color-tuning (white-light to purplish-pink and to pink) characters strictly relative to the Sm³⁺doping content and the λ_{ex} wavelength. Further using the **PVK@1** film (10:1; wt/wt) with the straightforward white-light (Φ_{PL} % 5.8%) as the emitting layer, its single-component solution-processed WPLED gives the electroluminescent performance (L_{max} of 157 cd/m², η_{max} of 0.65 cd/A and the white-light-emitting stability) satisfactory enough for portable full-color flat displays.

1. Introduction

Organo-Ln³⁺ complexes' luminescence has received considerable attention because of its Ln³⁺-specific high color-purity phosphorescence [1,2] with theoretically 100% inner quantum efficiency, giving a particular opportunity to optoelectronic devices [2–6]. In this perspective, compared with concerted efforts to purity-monochromatic (typically Tb³⁺-centered green-light [7–9], Eu³⁺-centered red-light [10] or Nd³⁺/Yb³⁺/Er³⁺-centered near-infrared-light [11]) organic/polymer light-emitting diodes (OLEDs/PLEDs), the realization of reliable panchromatic ones or white OLEDs/PLEDs (WOLEDs/WPLEDs) based on organo-Ln³⁺ complexes significantly lags far behind [12–14], which should attribute to their complicated white-light integration during electric-driven process. Nonetheless, in contrast to non-organo-Ln³⁺ counterparts [15,16] strictly relative to ligand-fielded spectroscopic properties toward WOLEDs/WPLEDs, the Ln³⁺-emissive visible color-primaries [1,2] are advantageous of less perturbation from external stimulations (ligand/electric-field, pH or temperature, etc.). And clearly, from the viewpoint of white-light production, the dichromatic strategy should be more easily-gone [17] than the trichromatic- or tetrachromatic-integrated one with conceivably intractable energy transfers between multiple color-primaries.

As a matter of fact, contributing to the Laporte- and spin-allowed ligand-centered transition (⁰S → ¹S) followed by the inter-system crossing (ISC; ¹S → ¹T) and the ¹T → Sm³⁺* transfer [18,19], the subsequent Sm³⁺-centered orange-light *hyper*-sensitive at 650 nm (⁴G_{5/2} → ⁶H_{9/2} transition) can be efficiently sensitized from one certain organo-Sm³⁺ complex. Further focusing on volatile organo-Sm³⁺ complex by the vacuum-deposition [21–25] or doping of organo-Sm³⁺ complex into a host (small-molecule [26,27] or polymer [28,29]) by the solution-processed procedure, their OLEDs/PLEDs with the desirable

Sm³⁺-centered orange-light have been envisioned. However, to the best of our knowledge, the generation of WOLEDs/WPLEDs using organo-Sm³⁺ complex as the color-primary component, is very rare [30], despite the theoretically expectable white-light [17] capable of a blue-*plus*-orange combination. For example, as to the pioneering WOLED [30] fabricated with NPB-[Sm(DBM)₃(phen)] (NPB % *N,N'*-di (naphthalen-1-yl)-*N,N'*-diphenyl-[1,1'-biphenyl]-4,4'-diamine, DBM % dibenzoylmethane; phen % 1,10-phenanthroline) *co*-deposited emitters, although its electroluminescent white-lights (CIE chromatic coordinates *x* % 0.32–0.28, *y* % 0.28–0.33) are stable and voltage-independent, the white-lights' integration is highly responsible with the unmanageable NPB-[Sm(DBM)₃(phen)] exciplex's color-compensation. And more unfortunately, besides the vacuum-deposition high-cost, its electroluminescent performance (L_{max} % 142 cd/m² and η_{max} % 0.17 cd/A) is unsatisfactory, and even inferior to that (L_e > 150 cd/m² and η_c > 0.5 cd/A) required for portable full-color flat displays [31]. Herein, from a cost-effective perspective, a conceptual approach to doping of specific organo-Sm³⁺ complex into PVK for the solution-processed WPLED is provided. On one hand, the blue-light of PVK could smoothly be color-compensated with Sm³⁺-centered orange-light toward the direct white-light production [17]. Moreover, the doping system endows PVK-assisted good hole-transporting and excellent physical properties [32]. Importantly, its single-component and solution-processed WPLED with a significantly simplified device structure, can be expected, which characteristic of white-light stability and cost-effectiveness, should give a new avenue for portable full-color flat displays [31].

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2. Experimental

The information of starting materials and characterization methods was depicted in [Electronic Supporting Information](#) (ESI). The pyrazolone ligand **Htba-PMP** was synthesized from the nucleophilic replacement reaction of 1-phenyl-3-methyl-pyrazolone-5 (**PMP**) and *tert*-butylacetyl chloride in the presences of $\text{Ca}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$ as the literature [12]. The ancillary ligand **5-Br-2,2'-bpy** (**5-Br-2,2'-bpy**) was obtained from the Stille coupling reaction [33] between 2, 5-dibromopyridine and 2-(tributylstannyl)pyridine in the presence of $\text{Pd}(\text{PPh}_3)_4$ (0).

2.1. Synthesis of the binary tris-pyrazolate-Sm³⁺ complex [Sm(tba-PMP)₃(5-Br-2,2'-bpy)] (**1**)

To a stirred MeOH solution (20 mL) containing the pyrazolone ligand **Htba-PMP** (0.6 mmol, 0.164 g), an equimolar amount of anhydrous NaOH (0.6 mmol, 0.024 g) was added, and the resultant mixture was reacted at room temperature for 3 h. Another MeOH solution (15 mL) containing $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ (0.2 mmol, 0.073 g) and **5-Br-2,2'-bpy** (0.2 mmol, 0.047 g) was added, and the resulting mixture was refluxed under a N_2 atmosphere for another 3 h. After cooling to room temperature, the obtained clear solution was filtered, and left to stand for several days to afford the microcrystalline product. For complex [Sm(tba-PMP)₃(5-Br-2,2'-bpy)] (**1**): Yield: 0.163 g, 68%. Anal. Calcd for $\text{C}_{58}\text{H}_{64}\text{N}_8\text{O}_6\text{BrSm}$: C, 58.08; H, 5.38; N, 9.34%. Found: C, 58.01; H, 5.42; N, 9.38%. FT-IR (KBr, cm^{-1}): 2953 (w), 2361 (w), 1636 (w), 1609 (s), 1593 (s), 1582 (s), 1533 (w), 1489 (s), 1437 (m), 1395 (w), 1368 (m), 1314 (w), 1275 (w), 1229 (w), 1074 (m), 1022 (w), 1003 (m), 908 (w), 841 (w), 810 (w), 789 (w), 752 (vs), 692 (m), 650 (m), 631 (w), 598 (w), 511 (w). ESI-MS (in MeCN) m/z : 1199.33 (100%), [M]⁺. The synthesis and characterization of the other two referenced complexes [Gd(tba-PMP)₃(5-Br-2,2'-bpy)] (**2**) and [La(tba-PMP)₃(5-Br-2,2'-bpy)] (**3**) are described in the [Electronic Supporting Information](#).

2.2. Synthesis of PVK@1 films blending from PVK and complex 1 with different mass ratios

To a stirred toluene solution (30 mL) containing the commercial PVK (M_w 9 $\times 10^4$ g/mol; PDI 1.5) and complex **1** with a stipulated mass ratio (wt/wt; 10:1 or 10:2.5) was added, and the resultant mixture was continuously stirred at 45 °C overnight. After 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 **PVK@1** films (wt/wt; 10:1 or 10:2.5): Yield: 95% (10:1); 98% (10:2.5). Representative FT-IR (KBr, cm^{-1}): 3060 (w), 3043 (w), 2972 (w), 2930 (w), 2904 (w), 1622 (m), 1618 (m), 1598 (m), 1584 (m), 1485 (s), 1453 (vs), 1408 (w), 1404 (w), 1396 (w), 1370 (w), 1333 (s), 1325 (s), 1259 (w), 1236 (m), 1226 (s), 1158 (s), 1125 (m), 1076 (m), 1066 (m), 1058 (m), 1027 (m), 1003 (m), 965 (w), 926 (w), 897 (w), 844 (w), 812 (w), 745 (s), 721 (s), 697 (w), 679 (w), 672 (w), 660 (w), 648 (w), 626 (w), 618 (w), 606 (w), 563 (w), 509 (w), 475 (w).

2.3. WPLEDs' fabrication and characterization

Using the synthesized **PVK@1** film (10:1, wt/wt) with the straightforward solid-state white-light as the emitting layer, its single-component WPLED configured with ITO/PEDOT:PSS (40 nm)/**PVK@1** (90 nm)/TPBi (30 nm)/LiF (1 nm)/Al (100 nm) was fabricated through a typically solution-processed procedure. In these materials, ITO (indium tin oxide) was the coated glass substrate, and PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)) functions as the hole-injecting material. TPBi (1, 3, 5-*tris*(2-*N*-phenylbenzimidazolyl)) was used 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, photophysical and electrochemical properties of the binary tris-pyrazolate-Sm³⁺ complex 1

As shown in [Scheme 1](#), through the reaction of $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$, **5-Br-2,2'-bpy** and the pyrazolone ligand **Htba-PMP** treated with an equimolar amount of anhydrous NaOH, the binary tris-pyrazolate-Sm³⁺ complex [Sm(tba-PMP)₃(5-Br-2,2'-bpy)] (**1**) was self-assembled in a receptive yield of 68%. For reference, the other complexes [Gd(tba-PMP)₃(5-Br-2,2'-bpy)] (**2**) and [La(tba-PMP)₃(5-Br-2,2'-bpy)] (**3**) were obtained from the same way as complex [Sm(tba-PMP)₃(5-Br-2,2'-bpy)] (**1**) except that $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ (0.2 mmol; 0.074 g) or $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$ (0.2 mmol; 0.071 g) while not $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ (0.2 mmol, 0.073 g) was used, respectively.

The three binary tris-pyrazolate-Ln³⁺ complexes **1–3** soluble in common organic solvents, were well characterized by EA, FT-IR, ¹H NMR and ESI-MS. Especially in the ¹H NMR spectrum of the *anti*-ferromagnetic [La(tba-PMP)₃(5-Br-2,2'-bpy)] (**3**), the combined proton resonances (δ 8.82–0.96 ppm) of both the deprotonated ligand (tba-PMP) and the ancillary ligand **5-Br-2,2'-bpy** in a stipulated molar ratio of 3:1, confirm its desirable binary tris-pyrazolate-La³⁺ component [34]. Moreover, the absence of the originally tautomerism-enolic ¼ C–OH proton signal (δ 14.19 ppm) of the **Htba-PMP** ligand should be arisen from the La³⁺-coordination. Furthermore, the ESI-MS result of the complexes **1–3** exhibit a strong mass peak at m/z 1199.33 for [Sm(tba-PMP)₃(5-Br-2,2'-bpy)] (**1**), 1207.34 for [Gd(tba-PMP)₃(5-Br-2,2'-bpy)] (**2**) or 1188.32 for [La(tba-PMP)₃(5-Br-2,2'-bpy)] (**3**) assigned to the major species [M]⁺, respectively. These observations further verify that every binary tris-pyrazolate-La³⁺ species of the complexes **1–3** is stable in the respective solution.

The photophysical property of the complexes **1–2** were explored in dilute MeCN solution at room temperature and 77 K, respectively, and summarized in [Figs. 1 and 2](#) and [1S](#). As shown in [Fig. 1S](#), the similar ligands-based absorption bands (251–253, 270–273 and 314–317 nm) of the complexes **1–2** are observed, where the significantly broadened UV–visible range (200–420 nm) relative to those (<350 nm) of the two (**Htba-PMP** and **5-Br-2,2'-bpy**) free ligands, should be contributed from the enhanced π -conjugation upon Ln³⁺-coordination. Upon photo-excitation (λ_{ex} 340 nm) for [Sm(tba-PMP)₃(5-Br-2,2'-bpy)] (**1**), as shown in [Fig. 1](#), the strong Sm³⁺-centered characteristic emissions (569 nm (⁴G_{5/2} → ⁶H_{5/2} transition), 609 nm (⁴G_{5/2} → ⁶H_{7/2} transition), 651 nm (⁴G_{5/2} → ⁶H_{9/2} transition) and 706 nm (⁴G_{5/2} → ⁶H_{11/2} transition)) and the weak while detectable emission peaking at λ_{em} 422 nm are concurrently observed, exhibiting a bright orange-light with a CIE

PMP)₃(5-Br-2,2'-bpy)] (Ln $\frac{1}{4}$ Sm, **1**; Ln $\frac{1}{4}$ Gd, **2** or Ln $\frac{1}{4}$ La, **3**).

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

(Commission International De L'Eclairage) chromatic coordinate $x \frac{1}{4} 0.553$ and $y \frac{1}{4} 0.345$. For the dual-emitting complex **1**, the ligands-based residual visible ($\lambda_{em} \frac{1}{4} 422$ nm) emission should be assigned to the intra-ligands $\pi-\pi^*$ transition, and the hyper-sensitive peak at 651 nm from $^4G_{5/2} \rightarrow ^6H_{9/2}$ transition should be resulted from its low molecular symmetry [35]. Moreover, its dual-emissive nature can further be confirmed with the lifetimes-decayed combination of ligands-based fluorescence ($\tau \frac{1}{4} 1.46$ ns; $\lambda_{em} \frac{1}{4} 422$ nm) and Sm^{3b}-centered phosphorescence ($\tau \frac{1}{4} 50$ μ s of Sm^{3b}-based $^6H_{9/2}$; $\lambda_{em} \frac{1}{4} 651$ nm) from the same chromophores.

To address the sensitization mechanism of the Sm^{3b}-based complex **1**, the emissive property of the Gd^{3b}-based complex **2** as the reference in solution at room temperature or 77 K was also examined. For the Gd^{3b}-based complex **2**, contrary to the ligands-based fluorescence ($\lambda_{em} \frac{1}{4} 422$ nm and $\tau \frac{1}{4} 2.49$ ns) at room temperature, it exhibits the typical 0-0 transition phosphorescence ($\lambda_{em} \frac{1}{4} 434$ nm and $\tau \frac{1}{4} 11.4$ μ s) at 77 K, from which, the triplet ($^3\pi-\pi^*$) energy level of 23,041 cm⁻¹ is reasonably estimated. Considering the UV-visible absorbance edge at $\lambda_{ab} \frac{1}{4} 362$ nm, the singlet ($^1\pi-\pi^*$)

Fig. 2. The schematic energy level diagram and possible energy transfer processes for the complex [Sm(tba-PMP)₃(5-Br-2,2'-bpy)] (**1**) and its blending PVK@1 films.

π^*) energy level of 27,624 cm⁻¹ is obtained. As shown in Fig. 2, the slightly smaller energy gap ΔE^1 (4583 cm⁻¹) between the $^1\pi-\pi^*$ and $^3\pi-\pi^*$ energy levels, endows a relatively effective ISC process according to the Reinholdt's empirical rule [36]. Therefore, the residual ligands-based emission ($\lambda_{em} \frac{1}{4} 422$ nm), together with the Sm^{3b}-centered sensitization through the large enough energy gap ΔE^2 (5117 cm⁻¹; $^3\pi-\pi^* \rightarrow ^4G_{5/2}$) between the ligands-based $^3\pi-\pi^*$ energy and the first excited state $^4G_{5/2}$ (17,924 cm⁻¹) of Sm^{3b} ion regulated with the Latva's empirical rule [37], should be the reason to the dual emissions for the complex **1**. Meanwhile, just through that efficient sensitization with the strong absorption followed by the $^1\pi-\pi^* \rightarrow ^3\pi-\pi^*$ ISC and the effective $^3\pi-\pi^* \rightarrow ^4G_{5/2}$ transition of Sm^{3b} ion, the complex **1** characteristic of the Sm^{3b}-centered orange-light, gives rise to a quantum efficiency (Φ_{sm}^1) of 5.2%. Noticeably, although the complex **1** shows a significantly lower photoluminescent output than those (up to 30%) of tris-pyrazolate-Tb^{3b}-complex analogues [7–9] due to the fact that the $^4G_{5/2} \rightarrow ^6H_{5/2}$ energy gap of Sm^{3b} ion is relatively small (~ 7400 cm⁻¹), which favors non-radiative decay processes [38], its Φ_{sm}^1 (5.2%) is receptive among previously reported organo-Sm^{3b}-complexes [20–28] for orange-light OLEDs.

To further elucidate the electrochemical behavior of the Sm^{3b}-based complex **1**, its cyclic voltammogram (CV) experiment was explored. As shown in Fig. 2S, based on an oxidation potential of 0.72 V versus Fc⁰/Fc, the HOMO level of the complex **1** is estimated to be 5.48 eV. By checking its lower-energy wavelength (362 nm, also Fig. 1S) at the UV-visible absorbance edge, the

energy gap E_g of 3.43 eV can also reasonably estimated. Therefore, the LUMO level of 2.05 eV for the complex **1** is actually calculated.

3.2. Color-tuning photophysical properties of **PVK@1** films blended from PVK and complex **1**

In consideration of the hole-transport-included good physical properties [32] of the blue-emitting PVK, the single-component hybrid films **PVK@1** were easily obtained from the physical mixing of the commercial PVK and the complex **1** with different mass ratios (wt/wt; 10:1 and 10:2.5). The PXRD patterns (Fig. 3S) of these two **PVK@1** films with different doping contents just exhibit the PVK-based amorphous peaks, indicating the low-concentration and homogeneous distribution of the complexes **1** into the polymeric PVK. Moreover, the TG analysis result (Fig. 4S) of the representative **PVK@1** film

(wt/wt; 10:1) shows the significantly improved thermal stability, given that a higher decomposition temperature interval of 448–460 C than that (282 C) of the complex **1**. In addition, the determined T_g of the representative **PVK@1** film (wt/wt; 10:1) can be up to 190 C, from which, it is of particular opportunity to utilize the **PVK@1** film (wt/wt; 10:1) as the ideal emitting layer for flexible WPLEDs.

The concentration-relative (wt/wt; 10:1 and 10:2.5) photo-luminescent properties of the **PVK@1** films at room temperature were explored, and summarized in Fig. 3. Importantly, the dichromatic- integration colors of these two **PVK@1** films are strictly enslaved to the excitation wavelength. Based on the significant overlap (also Fig. 1S) between the emission of the PVK host and the absorption of the complex

1 within the 280–320 nm range, λ_{ex} ¼ 280–320 nm with every 10 nm step-size should be used as the suitable excitation regime to realize the

Fig. 3. The λ_{ex} -dependent Emission spectra and corresponding CIE chromatic coordinates (inset) of the solid-state **PVK@1** films with different mass ratios (10:1 and 10:2.5; wt/wt) at room temperature.

Fig. 4. 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 η_{EQE} - L , η_p - L and η_c - L curves for the WPLED based on the **PVK@1** film (10:1; wt/wt).

dichromatic-modulated white-light especially in motivation with an effective Forster energy transfer [€ 12] from the PVK host to the complex **1**. Under the feeding mass ratio of 10:1, photo-excitation (λ_{ex} 280–320 nm) renders the **PVK@1** film the simultaneous emissions (Fig. 3a) of the PVK-based blue-light (422 nm) and the Sm^{3+} -centered orange-light. Interestingly, with the increase of the excitation wavelengths within the 280–320 nm region toward the maximum excitation wavelength (340 nm) of the complex **1**, the orange-to-blue relative intensity ratio increases, correspondingly, indicating that effective Forster energy transfer [12] from the PVK host to the complex **1** actually occurs. Besides all the resultant color-coordinates (**I-A-E**; x 0.275–0.301, y 0.220–0.232) located within the desirable white-light regime, their white-light quality of the dichromatic-modulation is reflected from the CCTs of 1762–2328 K and the CRIs within 77–91. Clearly, the warm-white-lights endowed with the CCTs (1762–2328 K) beyond the 2500–6500 K region, should be resulted from the typically dichromatic [7] while not trichromatic modulation for the **PVK@1** film (10:1; wt/wt). Nonetheless, among the stable white-lights with little color-coordinates shifts ($|\Delta x| < 0.03$, $|\Delta y| < 0.02$), the obtained quantum yield up to 5.8% for the best white-light point **I-E** (λ_{ex} 320 nm; x 0.301, y 0.232, CCT of 2328 K and CRI of 91) is at the top level within previously reported organo- Sm^{3+} -complexes [20–25] or organo- Sm^{3+} -doping systems [26–29] 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 for the **PVK@1** film (10:1; wt/wt) upon λ_{ex} 320 nm should unambiguously originate from both fluorescence and phosphorescence dichromatic incorporation.

Further with the increase of the Sm^{3+} -doping content up to 10:2.5 (wt/wt), it leads to the pronounced Sm^{3+} -centered orange-light. As shown in Fig. 3b, the relatively higher Sm^{3+} -doping content (10:2.5; wt/wt) renders the integrated colors significantly deviated from the white-light regime, exhibiting λ_{ex} -regulated purplish-pinks (**II-A-B**; the CIE chromatic-coordinates x 0.406–

0.411, y 0.267–0.268; the CCTs of 2231–2332 K and the CRIs of 89–90 with λ_{ex} 280–290 nm) to pink colors (**II-C-E**; the CIE chromatic-coordinates x 0.451–0.465, y 0.280–0.298;

the CCTs of 2233–2668 K and the CRIs of 87–90 with λ_{ex} 300–320 nm) also highly stabilized. It is worth noting that the residual blue-light species of the **PVK@1** film (10:2.5; wt/wt) decay with an almost constant lifetime (36 ns) to that (32 ns) of the **PVK@1** film (10:1; wt/wt), suggesting the excess amount (either 10:2.5 or 10:1) of the PVK host with saturation [12] of the dichromatic balance in the **PVK@1** films.

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

Considering the direct solid-state white-lights of the **1@PVK** film (10:1; wt/wt), its single-component solution-processed WPLED was fabricated, and the device performance was summarized in Fig. 4. On one hand, the deeper LUMO level (2.05 eV) of the complex **1** than that (2.00 eV) of PVK, and its shallower LUMO level (5.48 eV) than that (5.50 eV) of PVK, suggest the suitability of the PVK host when doped with the complex **1**. Meanwhile, according to the proposed energy level diagram for the WPLED shown in Fig. 4a, the two HOMO levels (5.50~5.48 eV) of PVK and the complex **1** are well between those (6.20~5.20 eV) of TPBi and PEDOT:PSS. Therefore, the injected electrons and holes could be trapped and recombined within the white-light-emitting species **PVK@1** (10:1, wt/wt).

As expected, the normalized electroluminescent spectra (Fig. 4b) of the WPLED based on the **PVK@1** (10:1, wt/wt) also exhibit the simultaneous emissions of PVK-based blue-light (λ_{em} 422 nm) and Sm^{3+} -centered (λ_{em} 651 nm) orange-light throughout the whole applied bias voltage range (6.0–12.5 V), leading to the integrated colors (CIE chromatic coordinates x 0.260–0.353, y 0.211–0.313) well within the desired white-light regime. However, in contrast to the λ_{ex} -relative monotonous increasing (also Fig. 3a) of the

orange-to-blue relative intensity ratio, the electroluminescent spectra are highly dependent on the applied bias voltages, where owing to the carrier-trapping mechanism during the electric-driven process, the orange-to-blue relative intensity ratio increases first and insistently decreases after 10.0 V. As shown in Fig. 4c, after the turn-on voltage (V_{on} at 1 cd/m²) of 6.0 V, the WPLED keeps stable in the 6.0–10.0 V range, both the luminance (L , cd/m²) and the current density (J , mA/cm²) monotonously increase, and a L^{Max} of 157 cd/m² is achieved at 10.0 V with a current density of 570 mA/cm². Under the stable premise, as shown in Fig. 4d, with the an increase of the applied bias voltage or the luminance, all the efficiencies (η_c , η_p , and η_{EQE}) increase first and insistently decrease with the η^{Max}_c of 0.65 cd/A, the η^{Max}_p of 0.25 lm/W and the η^{Max}_{EQE} of 0.5% at 8.0 V (L ¼ 66 cd/m²), respectively. Upon the applied bias voltage up to 10.0 V, the heavy efficiency-roll-offs with the η_c ¼ 0.27 cd/A, the η_p ¼ 0.09 lm/W and the η_{EQE} ¼ 0.22% of the WPLED are observed, which should mainly be attributed to Sm³⁺-centered phosphorescence lifetime being too long [26]. Nonetheless, the single-component WPLED's performance reforms with almost three times efficiencies (the η^{Max}_c of 0.65 cd/A, the η^{Max}_p of 0.25 lm/W and the η^{Max}_{EQE} of 0.5%) to those of previously organo-Sm³⁺-based WOLEDs [30], which together with the white-light-emitting stability, is satisfactory enough to the requirements for portable full-color flat displays [31]. Further increasing the applied bias voltage (>10.0 V), its significantly inferior performance should be attributed to the aging of the WPLED.

4. Conclusions

In summary, through the self-assembly of the pyrazolone ligand **Htba-PMP**, SmCl₃·6H₂O and the ancillary ligand **5-Br-2,2'-bpy**, the binary *tris*-pyrazolate-Sm³⁺ complex [Sm(tba-PMP)₃(5-Br-2,2'-bpy)] (**1**) with efficient orange-light was obtained. When doping of the complex **1** into the PVK host, exhibit the dichromatic color-tunable (white-light or purple-light) characters. Further utilizing the **PVK@1** film (10:1; wt/wt) with the straightforward white-light as the emitting layer, its single-component WPLED gives the good electroluminescent performance (L^{Max} of 157 cd/m², η^{Max}_c of 0.65 cd/A and the white-light-emitting stability), which, satisfactory enough for portable full-color flat displays, could be further improved after the following optimizations of both the organo-Sm³⁺ complex structure and the WPLED's procedure.

Declaration of competing interest

We promise that this work is original, unpublished even not being considered elsewhere, and we declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jlumin.2020.117054>.

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