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Crown-ether modified thermally evaporated perovskite light-emitting devices with increased operational stability



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ABSTRACT

Great progress has been made in the all-inorganic perovskite light-emitting device (PeLED) by thermal evaporation. However, the low operational stability of the PeLEDs by thermal evaporation is still a challenge to limit its further practical application. In this work, crown ether was introduced as the interface layer between hole transport layer (HTL) and thermally evaporated CsPbBr₃ emissive layer (EML). It is found that the crown ether could not only increase the conductivity of HTL, passivate the nonradiative traps but also control the formation of the insulating Cs₄PbBr₆ in the EML. Consequently, the current density was evidently improved with increased brightness and current efficiency. More importantly, the working stability was also greatly prolonged due to the suppressed nonradiative defects as well as joule heating. The champion PeLED achieved a turn-on voltage of 2.9 V, a maximum brightness of $15,717 \text{ cdm}^{-2}$, a current efficiency of 3.66 cdA^{-1} , an external quantum efficiency of 1.02%. More importantly, the control devices. Our findings would shed light on revealing the factors to improve operational stability of PeLED devices.

thickness of perovskite emission layers. In addition, the commercialized

PeLEDs) have experienced a rapid improvement with external quantum efficiency (EQE) surpassing 8% [6,17]. However, relative to the rapid

improvement in the efficiency of PeLEDs, its stability is somewhat lagging behind to meet the requirements for practical application.

Compared with TE-PeLEDs, the working stability of PeLEDs with other structures has made great progress [26,27]. To improve the stability of

PeLED is still a crucial challenge. Generally speaking, there are three main factors that affect the stability of the perovskite layer: 1) the

inherent defects of the perovskite layer itself [28-30]; 2) the migration

of halide ions under the action of electric field will also cause more

Recently, the performance of thermally evaporated PeLEDs (TE-

thermal evaporation could endow patterning easily [25].

1. Introduction

Inorganic metal halide perovskites have improved tolerance to humidity [1], high color purity [2], high photoluminescence quantum yields (PLQYs) [3], feasible spectral tunability [4] as well as easily fabricated with mature vacuum vapor deposition [5–18], which make them very promising candidates in display and lighting [19–22]. For the most efficient inorganic perovskite light-emitting device (PeLED), they are fabricated by solution process. However, the raw inorganic perovskite materials such as PbCl₂, CsBr, CsCl suffer from low solubility [23, 24], hindering the development of full-color all-inorganic PeLEDs. In contrast, the thermal vapor deposition could avoid the utilization of solvents and solubility limitation, resulting in a controllable and precise

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Fig. 1. (a) Device structure of the PeLED; (b) EL spectra; (c) J-V curves; (d) L-V curves; (e) CE-V curves and (f) EQE-V curves for the PeLEDs with different 18-Crown-6 modifications.

defects [31–34]; 3) Joule heat caused by the mismatched energy level alignments and different conductivity of the charge transport layer [35–38], further resulting in the carriers accumulation at the interface and accelerating the degradation of perovskite [39-42]. For CsPbBr₃ based TE-PeLEDs, the luminescent shallow states originated from the grain boundaries can be well passivated by the photo-inactive Cs₄PbBr₆ merely via tuning the CsBr/PbBr2 ratio. Gao et al. [16] have constructed a CsPbBr₃|Cs₄PbBr₆ host-guest composites and found that both the radiative recombination and stability could be improved significantly by the Cs₄PbBr₆ host. Du et al. also confirmed the CsBr/PbBr₂ ratio related electroluminescent performance by carefully controlling the CsBr/PbBr₂ ratio to realize spatial confinement of the Cs₄PbBr₆ to CsPbBr₃, achieving an outstanding EQE of 8% and working lifetime of 483 min at an initial brightness of 100 cd/m² [6]. However, it should be stressed that the less conductive Cs₄PbBr₆ may adversely affect device stability due to its poor charge transport properties. Qin et al. improved device operational stability significantly by replacing partial CsBr with NaBr to suppress the formation of the insulating Cs₄PbBr₆ phase [5]. Interfacial defects passivation would be another effective methodology to both improve the optoelectrical performance and device stability. Adopting NiO_v as a benign interface. Li et al. realized a brighter PeLED with EOE reaching 3.26% [10]. Kim et al. employed the MgCl₂-doped

polyethylene oxide (PEO) to passivate the interfacial defects and overcome the electrically insulating nature of PEO. The achieved champion device showed an EQE of 7.6%, brightness of 6887 cd/m² and a half-luminance lifetime of 390 s at L_0 of 100 cd/m² [8]. In our previous work, we also observed improved working duration of the PeLEDs by passivating the interfacial defects with ammonium halides and 3-amino-1-propanol [17,18]. More importantly, we found that the 3-amino-1-propanol could promote the formation of the Cs₄PbBr₆ and affect the composition of the perovskite. These results enlighten us that proper interlayer may not only passivate the interfacial traps but also control the formation of the Cs₄PbBr₆ to achieving a long working stability. Keeping this in mind, the interlayer with interaction of the Cs^+ , Pb^{2+} cations would be potential interlayers to meet the mentioned above requirements. Previous research found that crown-ether could interact with the meatal cations, which may affect the interaction between perovskite precursor materials during the crystallization process [21,43, 44]. However, the role of crown-ether as the interlayer in TE-PeLEDs remain largely unexplored.

Herein, 18-Crown-6 was introduced between the hole transport layer and the light-emitting layer through interface engineering. It is found that 18-Crown-6 can not only improve the conductivity of PEDOT:PSS and passivate surface defects, but also inhibit the formation of Cs_4PbBr_6 during the crystallization process. We also found the content of Cs_4PbBr_6 plays a decisive role in the operation stability of the device. Through further optimization, we obtained a high-performance PeLED with a lifetime of more than 10 h, a turn-on voltage of 2.9 V, a maximum luminous brightness of 15,717 cdm⁻², a current efficiency of 3.66 cdA⁻¹, and an external quantum efficiency of 1.02%. Our work has certain guiding significance for exploring the factors that affect the operational stability of PeLED devices.

2. Experimental section

2.1. Materials and method

Cesium bromide (CsBr) (99.9%) was purchased from Mreda. $PbBr_2$ (99.9%), TPBi and PEDOT:PSS were purchased from Xi'an Polymer Light Technology Corp. 18-Crown-6 was purchased from Macklin. The 18-Crown-6 ethanol solution is prepared by putting a quantitative 18-Crown-6 solid in absolute ethanol and shaking it sufficiently.

2.2. Film and device fabrication

The light-emitting layer (EML) is composed of CsPbBr3 which was prepared by vacuum thermally evaporating CsBr and PbBr₂. First, the fresh commercial ITO-coated glass was cleaned with ionized water and ethanol. Afterwards, the substrates were dried in a nitrogen environment with a N2 blower. Next, the ITO-coated glass was UV-ozone treated for 25 min. PEDOT:PSS was spin-coated on the ITO-coated glass at 3000 rpm for 30 s by the spin coater and then placed on a hotplate for annealing at 140 °C for 15 min in air. When the substrate temperature cooled down, 18-Crown-6 was spin-coated on the substrate at 4000 rpm for 30 s and annealed at 100 °C in air for 15 min. Then the substrate was transferred to a vacuum chamber (QHV-R20) for deposition of CsBr and PbBr₂ with rates lower than 1.5 Å/s and 0.6 Å/s, respectively. The Cs/Pb ratio was determined according to the XPS results. During this process, the substrate temperature kept at 100 °C and the nitrogen pressure in the vacuum chamber was lower than 5×10^{-4} Pa. When desired thickness was achieved, the perovskites were then annealed at 110 °C for 30 min in nitrogen environment. Finally, the substrates were transferred into the vacuum chamber again for the sequential preparation of the TPBi (ETL), LiF and Al (cathode).

2.3. Optical and electrical measurements

The PL spectra of perovskite films were measured on a Hitachi fluorescence spectrometer F-7000. The absorption characteristics were recorded using a Persee T6 UV-vis spectrometer. The XPS spectra using Al K α excitation (ThermoFischer , ESCALAB 250Xi) were measured to investigate the chemical nature of PEDOT:PSS and perovskites. The EL spectra were collected using Ocean Optics USB4000 fiber spectrometer. Kinetics of the perovskite films were characterized by an Edinburgh FLS920 spectrometer using a 375 nm semiconductor laser excitation source. For fs-TA measurements, the seed light generated by the MAI TAI HP femtosecond oscillator (2.5 W, 800 nm, pulse width 100 fs) is incident on the SPFIRE ACE-35F1HP femtosecond amplifier Medium (pulse width<35 fs, 7 mJ@1 kHz, 800 nm), and produces a laser beam (800 nm, pulse width 40 fs, 1 kHz, 5 W). The beam is divided into two beams by a 5:5 beam splitter. One beam passes through the BBO frequency doubling crystal to generate the pump light and the other is focused into the sapphire crystal to produce white detection light (450-700 nm). The transient absorption signal was collected by the Ocean Optics spectrometer (HR4000). The current density, current efficiency and luminance of the device were measured by Keithley 2400 coupled with a luminance meter (KONICA MINOLTA LS-160). The EQE was further calculated from the current density, luminance and electroluminescence spectrum.

Table 1

Evolution of the Performance (Turn-on voltage, Maximum Luminance, Maximum CEs, and Maximum EQE) of PeLEDs with Different Concentrations of 18-Crown-6.

18- Crown-6 (mg/ml)	V _{on} (V)	L _{max} (cdm ⁻²)	L ^a (cdm ⁻²)	CE _{max} (cdA ⁻¹)	CE ^a (cdA ⁻¹)	EQE _{max} (%)
w/o	3.1	7949	$\begin{array}{c} 8076 \pm \\ 424 \end{array}$	1.88	$\begin{array}{c} 1.79 \pm \\ 0.16 \end{array}$	0.52
2	3.1	13,548	$13,524 \pm 1036$	2.25	$\begin{array}{c} \textbf{2.36} \pm \\ \textbf{0.35} \end{array}$	0.63
4	2.9	15,717	$\begin{array}{c} \textbf{15,520} \pm \\ \textbf{531} \end{array}$	3.66	$\begin{array}{c} 3.16 \pm \\ 0.48 \end{array}$	1.02
7	2.9	11,001	$\begin{array}{c} 11,362 \pm \\ 1679 \end{array}$	2.89	$\begin{array}{c} \textbf{2.86} \pm \\ \textbf{0.56} \end{array}$	0.81

^a The values presented are the mean values with their standard deviation (at least 5 samples were examined for each condition).

3. Results and discussion

We constructed the PeLEDs with a typical structure of ITO/PEDOT: PSS/Perovskite/TPBi/LiF/Al (Fig. 1a). The 18-Crown-6 was introduced between the perovskite layer (CsPbBr₃) and the hole transport layer (PEDOT:PSS) as the interface modification layer. In the case where different concentrations of 18-Crown-6 were introduced, the electrical performance of the device is shown in Fig. 1. When the concentrations of 18-Crown-6 were 2 and 4 mg/ml, the corresponding current density have been evidently improved in comparison to the reference device (Fig. 1c). Meanwhile, the turn-on voltage (Von) was reduced from 3.1 V for the control device to 2.9 V for the 18-Crown-6 modified devices. The control device exhibited maximum luminance of 7949 cdm⁻², the best current efficiency (CE) of 1.88 cdA^{-1} and the maximum EQE of 0.52%. The maximum brightness has been increased to 15,717 cdm^{-2} and the current efficiency and EQE are increased to 3.66 \mbox{cdA}^{-1} and 1.02% for the PeLED with 4 mg/ml 18-Crown-6 modification, respectively. When the concentration of 18-Crown-6 further increased to 7 mg/ml, not only the current density conversely reduced but also the maximum brightness as well as the efficiency decreased, perhaps due to the over-amount of 18-Crown-6. More detailed parameters are summarized in Table 1. All in all, 18-Crown-6 could make a remarkable improvement in the electrical performance of the device, and it has no effect on the electroluminescence (EL) spectra (Fig. 1b and S1). The peak wavelength of the spectra with or without 18-Crown-6 modification centered at around 520 nm stably, and the full width at half maximum (FWHM) achieved 18 nm. The color coordinates of the International Commission on Illumination (CIE) are (0.19, 0.60) (plotted in Fig. S1c) showing that the device has high color purity and realistic quality.

To clarify the important role of 18-Crown-6 on the enhancement of the device performance, we first investigated its influence on the physical properties of PEDOT:PSS. The introduction of 18-Crown-6 may have an impact on the conductivity and work function of the PEDOT: PSS. We first constructed a hole-only device ITO/PEDOT:PSS(40 nm)/HAT-CN(5 nm)/Al (Fig. S2) to explore the effect of 18-Crown-6 on the conductivity of PEDOT:PSS. As can be seen from the J-V curves, the calculated conductivity (σ_0) of the 18-Crown-6 modified PEDOT:PSS was 3.53 μ S • cm^{-1} according to the following equation:

$$I = \sigma_0 A V/d \tag{1}$$

Where d denotes the thickness of the PEDOT:PSS, A is the device area. While the pristine PEDOT:PSS exhibited a lower conductivity of 2.41 μ S • cm^{-1} . Considering that the conductivity mainly depended on the PEDOT to PSS ratio [45], we carried out the X-ray photoelectron spectroscopy (XPS) spectrum to make a deep insight of how the 18-crown-6 affect the conductivity of PEDOT:PSS. In the XPS spectrum of S(2p), the binding energy at 167.6 eV corresponds to PSS, and the broad binding energy peak at around 162–165 eV belongs to PEDOT. Obviously, the



Fig. 2. (a) J-V characteristics of hole-only device; (b) XPS spectra of S(2p) in PEDOT:PSS with and without 18-Crown-6; (c) and (d) AFM images of the PEDOT:PSS without and with 18-Crown-6.

relative amount of PEDOT in the 18-crown-6 modified PEDOT:PSS film has been promoted. Such change in this ratio may be because 18-Crown-6 can weaken the Coulomb attraction between the positively charged PEDOT chain and the negatively charged PSS chain, causing the PSS component in the film to be washed away under the interaction of ethanol as we illustrated in Fig. S3. It should be stressed that the 18-crown-6 rather than the ethanol played a critical role on the changing of PSS ratio. The quite similar S(2p) binding energies between the ethanol treated PEDOT:PSS and pure PEDOT:PSS in Fig. S4a could exclude the ethanol interaction on the changes of the PSS amount. Meanwhile, we performed atomic force microscopy (AFM) measurements to investigate the influence of 18-crown-6 on the film morphology. As shown in Fig. 2c and Fig. S5, the quite similar island morphology for the pure PEDOT:PSS and ethanol treated PEDOT:PSS could provide another evidence that the ethanol played little role on the conductivity of PEDOT:PSS. In contrast, the island morphology became obscured covering with a quasi-continuous granular-aggregated 18-crown-6 layer with a slightly increased RMS of 2.63 nm (Fig. 2d). Moreover, we performed ultraviolet photoelectron spectroscopy (UPS) tests on the PEDOT:PSS films with 18-Crown-6 and without 18-Crown-6 (Fig. S4b). Fairly similar secondary-electron cutoffs mean that 18-Crown-6 does not change the work function of the hole transport layer. Overall, the introduction of 18-Crown-6 could increase the conductivity of PEDOT:PSS which would be one possible reason for the increased current density of the PeLEDs.

The chemical and physical characteristics of the underlayer would have an important impact on the perovskite layer. Hence, we further explored the effect of 18-Crown-6 on the optical physical properties of the perovskite films. Fig. 3a shows that regardless of whether there are 18-Crown-6 modified perovskite films, their absorption spectra have peaks at 315 nm and 520 nm. These two peaks correspond to Cs₄PbBr₆ and CsPbBr₃ in the film, respectively. In contrast to the strong and sharp Cs₄PbBr₆ absorption peak for the original perovskite film, the peak value of Cs₄PbBr₆ decreased significantly after 18-Crown-6 modification which indicates that 18-crown-6 could inhibit the formation of Cs₄PbBr₆ during the crystallization process. To verify this conclusion, we further performed XRD on the perovskite films with and without 18-Crown-6 modification (Fig. 3c). Clearly, both the perovskite films contained Cs_4PbBr_6 and $CsPbBr_3$ phase with diffraction peaks at $2\theta = 13.01$, 20.45, 25.88, and 31.31° for Cs_4PbBr_6 [46] and that at 15.40° for CsPbBr₃ phase (PDF#18-0364). For the 18-crown-6 modified perovskite sample, all the peak diffraction of Cs₄PbBr₆ were significantly reduced. Instead, increased diffraction peaks of CsBr $2\theta = 29.69^{\circ}$ and CsPbBr₃ at $2\theta = 15.40^{\circ}$ were obviously observed. These results can clearly confirm that 18-Crown-6 inhibited the conversion of CsPbBr3 to Cs4PbBr6 even under the CsBr rich condition, which coincide well with the absorption results. The PL spectra were shown in Fig. 3b, the PL intensity of the perovskite film with 18-Crown-6 has an obvious improvement compared with the original perovskite film with PLQY increased from 2.4% to 6.7%. The PL spectra for both samples exhibited almost similar FWHM $(\sim 18 \text{ nm})$, indicating that the addition of 18-Crown-6 did not affect the color purity of CsPbBr₃ film. At the same time, time-resolved photoluminescence spectra (Fig. S6) also showed that the exciton lifetime after 18-Crown-6 modification has also been improved. It is widely known that the Cs₄PbBr₆ could passivate the nonradiative traps which will enhance the PL intensity [16]. For our samples, the 18-Crown-6 modified film has a reduced Cs₄PbBr₆ content, but its PL intensity was increased compared to the original perovskite film. This indicated that 18-Crown-6 also had the function of passivating interface defects. To gain deep insight on how 18-Crown-6 inhibited the generation of Cs₄PbBr₆ and passivated the defects, Fourier transform infrared spectroscopy (FTIR) test was done to explore the mechanism of the reaction of 18-Crown-6 with perovskite. As shown in Fig. S7, the absorption peak located at 1104 cm⁻¹ which can be attributed to C–O–C stretching vibration [47,48] exhibited a slight redshift to 1104 cm⁻¹ after the incorporation of CsBr, indicative of a weak interaction. In stark contrast,



Fig. 3. (a) UV–vis absorption spectra with and without 18-Crown-6; (b) PL spectra with and without 18-Crown-6; (c) X-ray diffraction patterns (XRD) of CsPbBr₃ perovskite film with and without 18-Crown-6; TA spectra as a function of wavelength and pump-detection delay time for perovskite films without (e) and with (f) 18-Crown-6.

an additional absorption peak at 1090 cm⁻¹ was observed in the 18-Crown-6/PbBr₂ mixture as well as 18-Crown-6/CsPbBr₃ mixture, which can be attributed to the chemical interaction between PbBr2 due to the Lewis base-acid interaction [49]. The interaction between 18-Crown-6 and Pb^{2+} as well as Cs⁺ may isolate the CsPbBr₃ and CsBr, thus hampering the formation of Cs₄PbBr₆ as revealed by the UV-vis absorption spectra. Additionally, it is well known that uncoordinated Pb atoms can induce nonradiative recombination. In our case, the oxygen atom in C-O-C group could donate a lone electron pair and then stabilize the uncoordinated positively charged Pb²⁺, eventually enhancing the radiative recombination. Femtosecond time-resolved transient absorption spectra (TAS) were recorded to further reveal the exciton bleach-recovery kinetics. Fig. 3d and e showed that the transient bleach minimum during which process the photoexcited carriers relax to the lowest energy sites appeared a redshift probably caused by the defect states [50,51]. The redshift of the 18-crown-6 modified perovskite is slightly smaller than that of neat perovskite. Meanwhile, the sample with 18-Crown-6 showed decreased band-tail states. The reduced redshift in the transient bleach minimum and band-tail states suggested an increased radiative transition probability and a decreased

nonradiative trap states which confirmed that 18-Crown-6 can effectively passivate the interface defects of the perovskite film [52]. The trap states density for the 18-Crown-6 modified perovskite film determined through the space charge limited current (SCLC) test (Fig. S8) is 6.80×10^{17} cm⁻³ which is obviously suppressed in comparison to that of pure perovskite film (~8.75 $\times 10^{17}$ cm⁻³), affirming the trap passivation effect from 18-Crown-6.

Considering that Cs_4PbBr_6 has much higher insulation compared with $CsPbBr_3$ phase, the increase of its content will have a certain impact on the carrier transport characteristics of the light-emitting layer [16]. Therefore, the suppression of Cs_4PbBr_6 may lead to improvement in the conductivity of the perovskite film. This may also be another reason why the current density of the device is increased after 18-Crown-6 modification. Combined with our conclusion above, the improvement in device performance is because 18-Crown-6 not only improves the conductivity of the hole transport layer (PEDOT:PSS), but also passivates the interface defects of the perovskite layer.

Benefiting from the defect-passivation effect and suppression of insulating Cs_4PbBr_6 , the operation stability for the PeLEDs with 18-Crown-6 could be expected to be improved due to the reduced



Fig. 4. (a) Absorption spectra of perovskite films with different CsBr/PbBr₂ ratios and with and without 18-Crown-6 modification; (b) Lifetime of the PeLEDs with different CsBr/PbBr₂ ratios and with and without 18-Crown-6 modification; (c) Evolution of the PL intensity for the freshly thermal-evaporated perovskite films under heating at 100 °C.

nonradiative defects and joule heating. To elucidate how the working lifetime evolved as the Cs₄PbBr₆ amount changes, we changed the CsBr/ PbBr₂ ratio of the perovskite films and measured the corresponding working stability of the PeLEDs. The CsBr/PbBr₂ ratios were determined by the XPS results. As shown in Fig. 4a, as the CsBr/PbBr₂ ratio varied from the 1.99 to the 2.24, the Cs₄PbBr₆ in the absorption increased gradually. For each ratio, the 18-Crown-6 modified perovskite films exhibit a decreased Cs₄PbBr₆ absorption peak, affirming the suppression of Cs₄PbBr₆ by 18-Crown-6 as mentioned above. The corresponding lifetime for the 18-Crown-6 modified PeLEDs are also prolonged from 0.22 h to 2.2 h (Cs/Pb = 1.91), 0.35 h to 11.8 h (Cs/Pb = 2.44) and 0.13 h to 6.7 h (Cs/Pb = 3.04). As well as we know, the lifetime of 11.8 h has been the longest among the reported PeLEDs despite with the moderate EL performance (as shown in Table S1). Although Cs₄PbBr₆ is gradually increasing, the lifetime of the device does not increase monotonously instead of a decrease at a high ratio. Heat-induced PL degradation would be one possible reason for these above decrease in lifetime since the insulating Cs₄PbBr₆ would cause accumulation of carrier interfaces and further generate more Joule heat. To prove that heating can affect the light emission of the perovskite film, we measured the PL evolution with time at a constant temperature of 100 °C. The freshly fabricated perovskite films showed an increase in PL when heating after 30 min and following a relatively rapid decrease (Fig. 4c). However, the 18-Crown-6 modified films exhibited a retard degradation, suggesting a better thermal stability of the perovskite films. In a word, the control of the proportion of Cs₄PbBr₆ has a critical influence on the working stability of the device.

4. Conclusions

In summary, stable and efficient thermally evaporated CsPbBr₃ PeLEDs have been realized through incorporating 18-crown-6 interface between HTL and emissive layer CsPbBr₃. The 18-crown-6 can not only improve the conductivity of the PEDOT:PSS by removing the lessconductive PSS component, but also suppress the formation of the insulating Cs₄PbBr₆ phase which enabled the higher current density. Moreover, the 18-crown-6 could passivate the nonradiative defects with brighter emission. Consequently, the PeLEDs exhibited an improved luminescence of 15,717 cd/m², a current efficiency of 3.66 cd/A and a prolonged lifetime of 11.8 h. Although the working stability of the device has been greatly improved, the performance of the device is not comparable to the analogues. This may be related to the poor PLQY of the perovskite emission layer. Interfacial strategies employing other passivation agents may be one plausible solution to further improve the PLQY and finally achieve a better comprehensive EL performance with better operational stability along with efficiency.

Author statement

Li'ang Zhao and Yuan Zhang: Methodology, Formal analysis, Writing - Original Draft. Kai Sun: Characterization. Li Song: Conceptualization, Writing - Original Draft. Hao Xu: Visualization. Xiaoyang Guo: Conceptualization, Writing - Review & Editing, Funding acquisition. Shu Xu: Funding acquisition. Yuanqin Xia: Supervision. Yongsheng Hu and Fengying Ma: Writing - Review & Editing.

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.

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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.2022.119317.

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