

1 **Enhanced the luminescent performance of CsPbI₃ quantum**
2 **dot-embedded borosilicate glass by controlling**
3 **crystallization using Dy³⁺ ions as nucleating agent for remote**
4 **color-tunable LEDs**

5 Chaotong Zhou¹, Yu Ma¹, Fan Jiang¹, Guoying Zhao^{1*}, Jingshan Hou¹, Yufeng Liu¹, Xin Qiao^{2*},
6 Zhongzhi Wang², Ji-Guang Li³, Yongzheng Fang^{1*}

7 ¹ *School of Materials Science and Engineering, Shanghai Institute of Technology, Shanghai 201418,*
8 *PR China*

9 ² *Baotou Research Institute of Rare Earths, Baotou, 014030, China*

10 ³ *Research Center for Functional Materials, National Institute for Materials Science, Tsukuba,*
11 *Ibaraki 305-0044, Japan*

12 **Corresponding author, E-mail addresses: zhaogy135@126.com; qiaoxinbt@163.com;*
13 *fyz1003@sina.com.*

14 **Abstract:** Different concentrations of Dy³⁺ and perovskite quantum dots (PQDs)
15 were simultaneously embedded in the B-Si-Zn glasses by melt-quenching and
16 heat-treatment subsequently. A battery of experimental results including TEM,
17 distribution of different elements, and photoluminescence prove that partial Dy ions
18 are successfully doped into CsPbI₃ and played different roles depending on the doping
19 concentration. When the Dy³⁺ concentration is circa 0.1mol%, Dy³⁺ as a nucleation
20 agent reduces the energy required for the precipitation and growth of perovskite
21 quantum dots, obtaining outstanding quantum efficiency of 31.82%. The excess Dy³⁺
22 supplement will prevent the mobility of PQDs elements. Based on the as-made glass
23 sample, the remote fluorescent films have been successfully prepared. A kind of
24 prototype lighting device was assembled, which demonstrated a high color rendering
25 index of 96.5 under the current of 20mA. Interestingly, by adjusting the concentration
26 of Dy³⁺, color regulation can be achieved from orange-red light to yellow-white light.

27 **Keywords:** CsPbI₃; Dy³⁺; Boron-silicate glass; Remote fluorescent films; High
28 quantum efficiency

29

30

1. Introduction

In recent years, inorganic cesium lead halide (CsPbX_3 , $\text{X}=\text{Cl}, \text{Br}, \text{I}$) perovskite quantum dots (PQDs) have attracted a lot of attention because of their excellent optical properties such as narrow full width at half maxima (FWHM), precisely tunable bandgap, large absorption intensity and high photoluminescence quantum yield (PLQY), which suggests great potential applications in optoelectronic fields including lighting, display as well as lasing^[1-4]. Unfortunately, colloidal CsPbX_3 PQDs generally suffer from poor long-term stability upon the impact of moisture, heat and light irradiation of their low formation energy and ionic crystal features^[5-7]. In previous studies, glass has become a well-regarded host for protecting perovskite quantum dots. The transparent glass matrix can cover the quantum dots, achieving good stability and maintaining the quantum dots excellent optical properties^[8-10].

Different to the wet-chemical synthesis route to fabricate colloidal CsPbX_3 PQDs, the nucleation mechanism and growth behavior of quantum dots are greatly restricted by the properties of mother glass melt, though it protects them from environmental induced degradation^[1,11,12]. During the heat treatment processing, the viscosity and rigidity of glass melt will hinder the mobility of Cs^+ , Pb^{2+} and X^- ions, which make it difficult to obtain the whole-family precipitation of CsPbX_3 PQDs^[13]. Consequently, how to realize controlled crystallization of quantum dots in glass remains challenging. Moreover, PLQYs of glass-stabilized CsPbX_3 PQDs are relatively lower than that of corresponding colloidal counterparts, especially CsPbI_3 , which becomes a major issue to obstruct the practical application in solid-state lighting. To address this problem, Chen et al introduced F^- ions into borosilicate glass, obtaining PLQY of 50% from CsPbI_3 ^[13]. Recently, the CsPbI_3 PQDs@glass has been prepared in our groups, and the highest PLQY value of glass stabilized CsPbI_3 reaches 17.1% by virtue of the regulation of glass grid structure^[1]. It is reported that the PLQY of pure CsPbI_3 PQDs@glass is only 4.2%^[14].

Another critical disadvantage of PQDs@glass is reabsorption between excitation and emission energy. In the current LEDs based on CsPbX_3 PQDs glass, it is necessary to mix different halogen synthesis glass powder to obtain a variety of multi-color converters by careful regulation^[15]. In view of wide absorption band of CsPbX_3 PQDs, the energy transfer of excitation photons among different color glass powder is inevitable. In addition, it is difficult to obtain an appropriate proportion of CsPbX_3 PQDs in glass powder and ultimately get a white light via excitation by blue-chip, leading to a completely complicated and inefficient process^[16,17]. The

1 existing technology is still not rid of the shortcomings of the dispensing LED package,
2 such as complex operation and low efficiency^[18]. Therefore, we need to synthesize a
3 CsPbX₃ PQDs glass that can both effectively improve the operability and also enable
4 better application in light-emitting diodes (LEDs). In this work, the remote
5 fluorescent film of a single system has been successfully prepared for effectively
6 solving the above problems.

7 From the above consideration, the rare earth ions, Dy³⁺ ions, were introduced
8 into CsPbI₃ PQDs embedded borosilicate glasses in present work. The reasons for
9 selecting Dy³⁺ ion are two-fold. Firstly, Dy³⁺ ion is a kind of glass network modifier,
10 which can break the tightness of glass network, improving the mobility of extrusive
11 Cs⁺, Pb²⁺ and I ions during precipitation processing^[1,19,20]. The homogeneous
12 distribution of Dy³⁺ ion is beneficial to the finely controlled nucleation and growth of
13 PQDs in glass host. Secondly, the yellow and blue color attributed to the f-f electronic
14 transitions of Dy³⁺ ion will compensate colorimetric absence of CsPbI₃ PQDs, for the
15 purpose of enhancing the luminescent performance^[21,22]. By adjusting the
16 concentration of Dy³⁺ dopants in glass matrix, the influence of Dy³⁺ dopants on
17 structure and optical properties of CsPbI₃ PQDs has been systematically studied to
18 explore its potential application in white LEDs. All the experimental results
19 demonstrate that this Dy³⁺ doped glass-stabilized CsPbI₃ PQD characterized with high
20 quantum efficiency, excellent physical/chemical stability and color tunability is a
21 promising converter candidate for remote white LEDs.

22 **2. Experimental Section**

23 Glass specimens with the nominal composition of
24 38SiO₂-29B₂O₃-16ZnO-9Cs₂CO₃-5.4PbI₂-10.8KI-xDy₂O₃ (x=0, 0.1, 0.3, 0.5, 0.7,
25 0.8, 1.0 mol%) were prepared by conventional melt-quenching. The raw materials
26 were prepared from high-purity SiO₂, B₂O₃, ZnO, Cs₂CO₃, PbI₂, KI and Dy₂O₃
27 powder. Well-mixed raw materials (15 g) were dissolved in a capped alumina crucible
28 and melted at 1200°C for 15 min under an ambient atmosphere. Then the molten glass
29 liquid was poured into a preheated copper plate to obtain precursor glass. Furthermore,
30 the CsPbI₃ PQDs@glass was successfully prepared through controllable in-situ glass
31 crystallization via heating at 480°C for 10 h. Finally, the as-prepared glass samples
32 were ground or polished to obtain a shape of 20×15×1.5 mm³ for subsequent
33 characterization.

34 The XRD patterns of the samples were recorded by X-ray diffraction (XRD)
35 system (Rigaku, Ultima IV, Japan) through a Cu K_α radiation source with a scan range

1 covered from 10 to 80° and a scan rate of 8°/min and 0.02°/step. The microstructure of
2 the sample was studied by TEM (JEM-2100F). The optical absorption spectra were
3 recorded at room temperature using a UV–visible–NIR spectrophotometer (Hitachi,
4 UH4150), working at 400–1800 nm. The photoluminescence properties (excitation
5 spectra, emission spectra, and temperature dependent photoluminescence spectra)
6 were measured by F-7000 spectrofluorometer equipped from Hitachi Instruments.
7 PLQY and fluorescent lifetime for the CsPbI₃ PQDs@glass samples were recorded on
8 an Edinburgh Instruments FS5 spectrofluorometer. All measurements were carried out
9 at room temperature. The color of emission light was determined by CIE 1931 (x, y)
10 chromaticity diagram.

11 Absolute photoluminescence Quantum yield (PLQY), defined as the ratio of
12 emitted photons to absorbed ones, was measured by a spectrofluorometer (FS5). An
13 integrating sphere was mounted on the spectrofluorometer with the entrance and exit
14 ports located in 90° geometry. The PQD sample was located in the center of the
15 integrating sphere. All the recorded spectroscopic data were corrected for the spectral
16 responses of both the spectrofluorometer and the integrating sphere. The responses of
17 the detecting systems (integrating sphere, monochromators and detectors) in photon
18 flux were determined using a calibrated tungsten lamp. Based on this setup, PLQY is
19 calculated based on the following equation

$$20 \quad \eta = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}} = \frac{L_{\text{sample}}}{E_{\text{reference}} - E_{\text{sample}}} \quad (2-1)$$

21 where η represents QY, L_{sample} the emission intensity, $E_{\text{reference}}$ and E_{sample} the
22 intensities of the excitation light not absorbed by the reference and the sample
23 respectively. The difference in integrated areas between the sample and the reference
24 represents the number of the absorbed photons. The emitted photons were determined
25 by integrating the related emission band.

26
27
28
29
30
31
32
33
34

3. Result and Discussion

3.1 Crystal structure identification

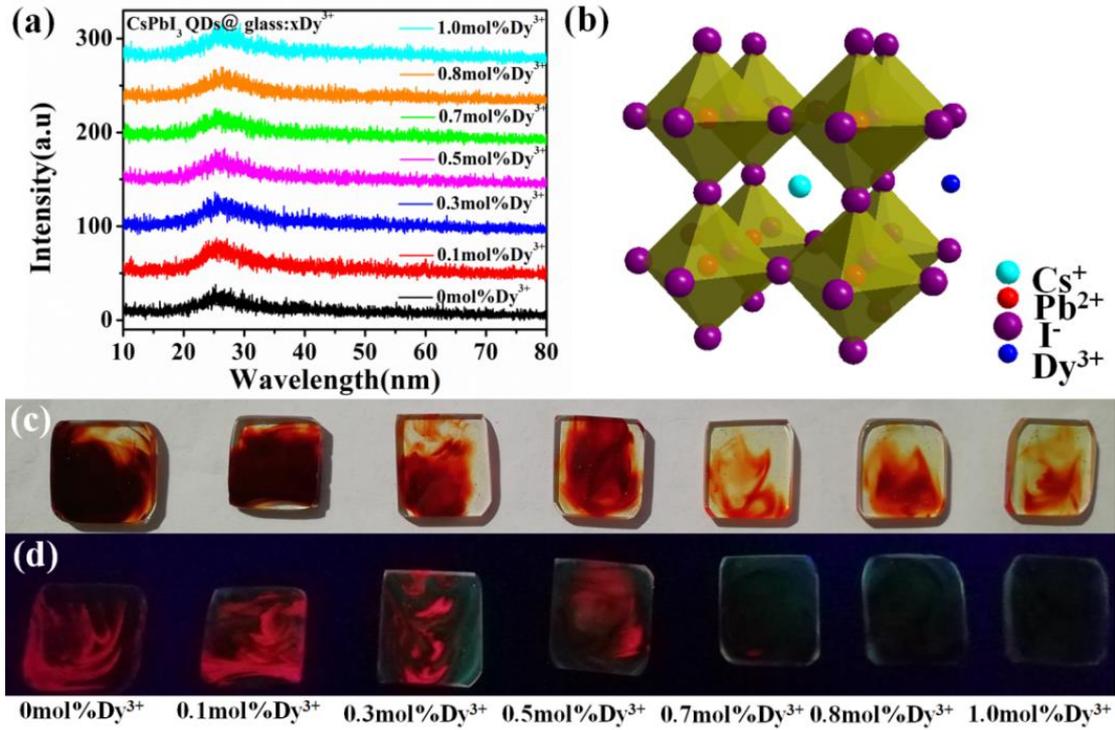
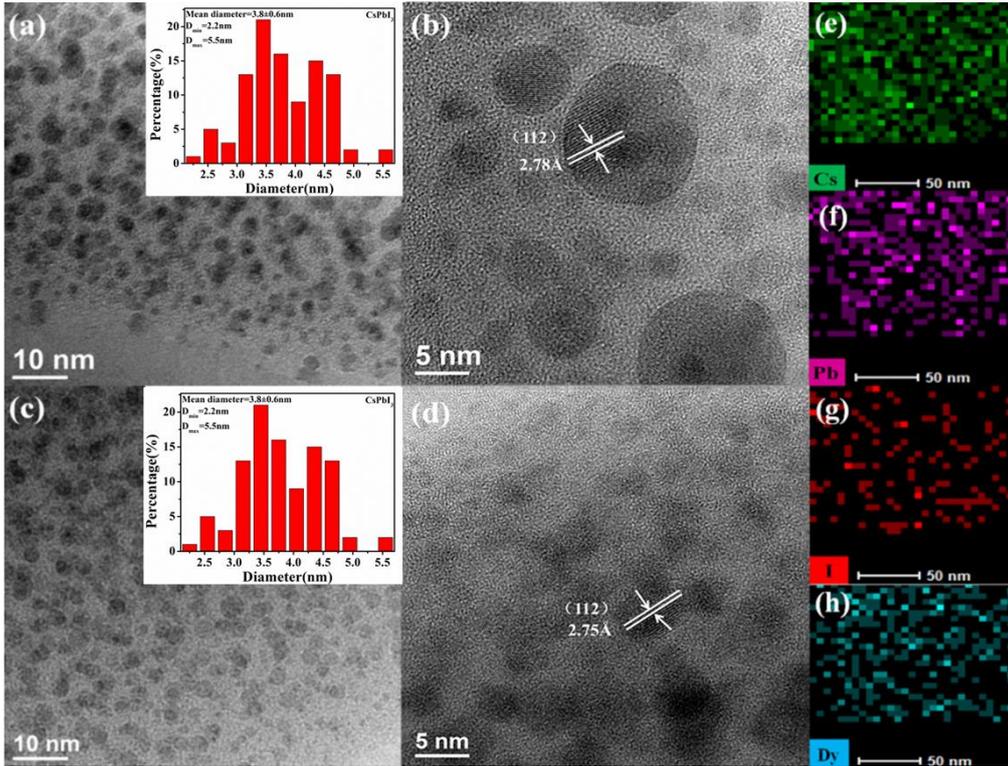


Figure 1. (a) XRD patterns of CsPbI₃ PQD@glasses with different Dy³⁺ ion doping concentrations; (b) crystal structure of CsPbI₃ PQD typical unit cell and the substitution of Dy³⁺; (c) photographs of CsPbI₃ PQDs@glass plates with different Dy³⁺ ion doping concentrations under daylight and (d) irradiation of a UV lamp.

XRD patterns of a series of CsPbI₃ embedded glass with different concentrations of Dy³⁺ are shown in Figure 1a. Evidently, the patterns exhibit a broad hump in the diffraction angle of 26°, indicating that the typical amorphous feature of glass samples [23,24]. No obvious diffraction peaks attributed to CsPbI₃ PQDs are observed in XRD patterns, which might be due to the trace amount of quantum dots embedded within glasses [1,25,26]. Fortunately, the bright red color of glass flakes under an ultraviolet lamp confirms the successful precipitation of CsPbI₃ PQDs in glass (Figure 1c). In fact, there is a faint yellow light under the naked eye, but due to the low doping concentration of Dy, the luminous efficiency is hardly high. By contrast, the light from quantum dots is more concentrated and sharper, therefore, it appears red in the glass eventually. Figure.1b demonstrates the unit-cell structure of the CsPbI₃ PQD. It consists of 12-coordinated Cs⁺ ions and 6-fold coordinated Pb²⁺ ions. With the increasing doping concentration of Dy³⁺ ions, the color of glass samples changed remarkably as shown in Figure 1c and d. It is indicated that the ligand surrounding Dy³⁺ ions has an important impact on the growth and photoluminescent behavior of

1 CsPbI₃ PQD.



2
3
4 **Figure 2.** HRTEM spectra of CsPbI₃ QDs glass without Dy³⁺ (a, b) and with 0.5 mol% Dy³⁺
5 doping (c, d); the inset of (a) and (c): the particle size distribution for CsPbI₃ PQDs in the
6 glass without Dy³⁺ and with 0.5 mol% Dy³⁺ doping, respectively; (e-h) Cs, Pb, I, Dy
7 elemental mappings.

8 In order to further explore the existential state of Dy³⁺ ions in glass,
9 high-resolution TEM (HRTEM) images of CsPbI₃ QDs glass without and with 0.5 mol%
10 Dy³⁺ doped samples are depicted in Figure 2. The clear lattice fringes with an
11 inter-planar distance of 2.78 Å evidence the successful precipitation of CsPbI₃ PQDs
12 with high-crystallinity, which corresponds to the (112) crystal facet. This value of
13 CsPbI₃ PQDs is decreased to 2.75 Å since the introduction of 0.5 mol% Dy³⁺ into
14 glass matrix. The ionic radius of Dy³⁺ in 6-fold coordination is 0.912 Å suggesting
15 substitution at Pb²⁺ (1.19 Å) sites in CsPbI₃ PQD^[27]. The much big size difference
16 between Dy³⁺ and Pb²⁺ in octahedral coordination gives reasonable evidence for the
17 reduced inter-planar distance of (112) crystal facet. Notably, Figure 2a demonstrates
18 the homogeneous distribution of PQDs with an average diameter of 3.8 nm. After the
19 introduction of Dy³⁺, the average diameter of PQDs was decreased to 3.4 nm in
20 Figure 2c. By comparison, the spot size in Figure 2c exhibits the relatively regular
21 distribution in Dy³⁺ ions doped glass sample.

22 The EDS mapping that includes Cs, Pb, I and Dy elements were carried out to

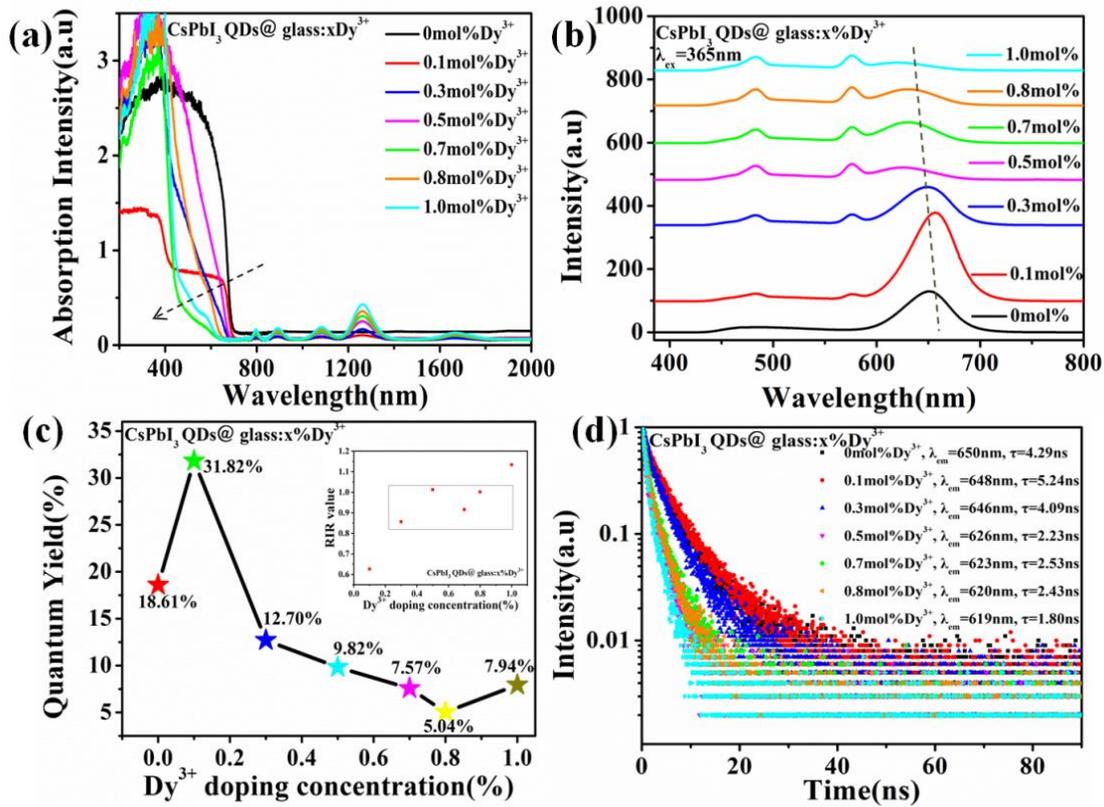
1 check the possible reaction between quantum dots and rare earth ions, as shown in
2 Figure 2e-h. It is clearly seen that these elements are homogeneously dispersed in host
3 glass. Nevertheless, the evidence that the overlap of the element distribution between
4 Dy and I is comparatively small manifests that partial Dy^{3+} ions are involved in
5 CsPbI_3 PQDs synthesis inevitably. As a result, there are two kinds of quantum dots in
6 glass host, that is, CsPbI_3 and CsDyI_3 . Dy_2O_3 as raw material is a glass network
7 modifier, which can break the chemical bonds of bridging oxygens during the glass
8 network forming processing. Therefore, the destruction of the ligand surrounding
9 around reduces the energy required for the precipitation of all elements, promoting the
10 formation of quantum dots [13,28]. Notably, the introduction of excessive Dy^{3+}
11 supplements in raw material will limit the growth of PQDs in glass. Dy^{3+} ions seem to
12 be an obstacle in the transmitting tunnel of all PQD elements. This can be explained
13 by the adverse impact of Dy^{3+} for the surrounding elements polymerization, leading to
14 hindering the mobility of extrusive Cs^+ , Pb^{2+} and I^- ions from grid. Besides, the
15 homogeneous distribution of Dy^{3+} in glass host is beneficial to guide to regular
16 arrangement of quantum dots.

17 *3.2 Luminescence Properties*

18 In order to clarify the fluorescence property of CsPbI_3 QDs glasses doped with
19 different concentrations of Dy^{3+} , the absorption and emission spectra were examined
20 and shown in Figure 3a-b, respectively. The absorption spectra of glass samples have
21 five sharp absorption peaks located at 800 nm, 896 nm, 1088 nm, 1271 nm and 1675
22 nm, which are characteristic absorption peaks of rare earth ion Dy^{3+} [20]. Moreover, a
23 wide absorption band peaked around 680 nm is attributed to CsPbI_3 PQDs[29].
24 Interestingly, the absorption cut-off edge is detected to shift to the ultraviolet sideband
25 with the increasing Dy^{3+} concentration, which is probably associated with the lower
26 PQDs concentration resulting from the inhibiting effect aroused by excessive Dy^{3+}
27 ions. Figure 2b exhibits the photoluminescence (PL) spectra of as-made samples
28 under excitation at 365 nm. Three emission peaks can be easily seen from PL spectra
29 except for the un-doped sample. The blue emission band peaked at 484 nm and
30 yellow emission band peaked at 576 nm are attributed to the 4f-4f electronic transition
31 $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ of Dy^{3+} ions, respectively. Besides, the red emission
32 band around 620-650 nm originates from direct exciton recombination[12]. Except for
33 the sample doped with 0.1 mol% Dy^{3+} ions, the peak wavelength of red emission shift
34 towards the shorter wavelength side until it nearly quenches as the concentration of
35 Dy^{3+} increases. Meanwhile, the intensity of red emission exhibits a similar change

1 tendency. Based on the above discussion, both sides of the introduction of Dy^{3+} ions
2 into glass system should be responsible for this phenomenon. It is reasonable to
3 conclude that there exists an optimal concentration of Dy^{3+} ions around 0.1 mol% in
4 glass, which can boost the migration of PQDs element by loosening the glass grid.
5 Dy^{3+} ion as glass network modifier breaks the bridging oxygen's links, as a result,
6 reduces the energy required for precipitation and nucleation of CsPbI_3 PQDs^[1,13].

7 The PL spectra reveal that the optimal Dy^{3+} doping concentration is circa 0.1
8 mol%. Correspondingly, the PLQY results also support this finding. [Figure 3c](#)
9 [exhibits the quantitative emission spectra of 0.1 mol% \$\text{Dy}^{3+}\$ \$\text{CsPbI}_3\$ quantum dot glass](#)
10 [and the reference sample and the corresponding absolute quantum yield, which was](#)
11 [measured at an excitation wavelength of 365nm](#). The dependence of absolute PLQY
12 values on the Dy_2O_3 content was recorded, as shown in [Figure 3c](#), which has a similar
13 tendency with CsPbI_3 QDs luminescence intensity. When Dy concentration is 0.1
14 mol%, the PLQY of red emission from PQDs embedded glass reaches the maximum
15 value that is 31.82%. The excess Dy offer results in a drop of PLQY, which further
16 evidences our insights of both sides. A similar change has also been detected in PL
17 decay curve measurements ([Figure 3d](#)). To gain more understanding of the ligand
18 surrounding Dy^{3+} in glass, the yellow-blue emission intensity (Y/B) ratio of Dy^{3+} was
19 calculated and exhibited in the inset of [Figure 3c](#). The $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ (yellow) transition
20 is electric dipole (ED) transition and hypersensitive in nature, while the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$
21 (blue) transition is magnetic dipole (MD) dominant. The intensity ratio of electric
22 dipole to magnetic dipole transitions has been used to measure the asymmetry and
23 degree of covalence of the local environment of Dy^{3+} ions^[30,31]. With the increasing
24 Dy^{3+} concentration, Y/B ratio roughly exhibits the increasing trend. A twofold increase
25 suggests the great change in ligand environment surrounding Dy^{3+} ions. It can be
26 concluded that a great number of Dy^{3+} ions are located inside the distorted iodine
27 octahedron, resulting in the formation of CsDyI_3 . The regular structure of quantum
28 dot and low covalence state of Dy^{3+} -I should be responsible for the low Y/B ratio
29 when the concentration of Dy^{3+} ion in glass is 0.1 mol%. After the excess amount of
30 Dy^{3+} ions were introduced into glass system, the structural tolerance capacity and low
31 content of perovskite quantum dot drive the doped Dy^{3+} into amorphous phase. As a
32 result, Y/B ratio is increased. [Figure 3d](#) exhibits the decay curves of CsPbI_3 PQDs in
33 glasses, Nanosecond lifetime confirmed the typical exciton recombination
34 characteristics of CsPbI_3 PQDs embedded in glass.

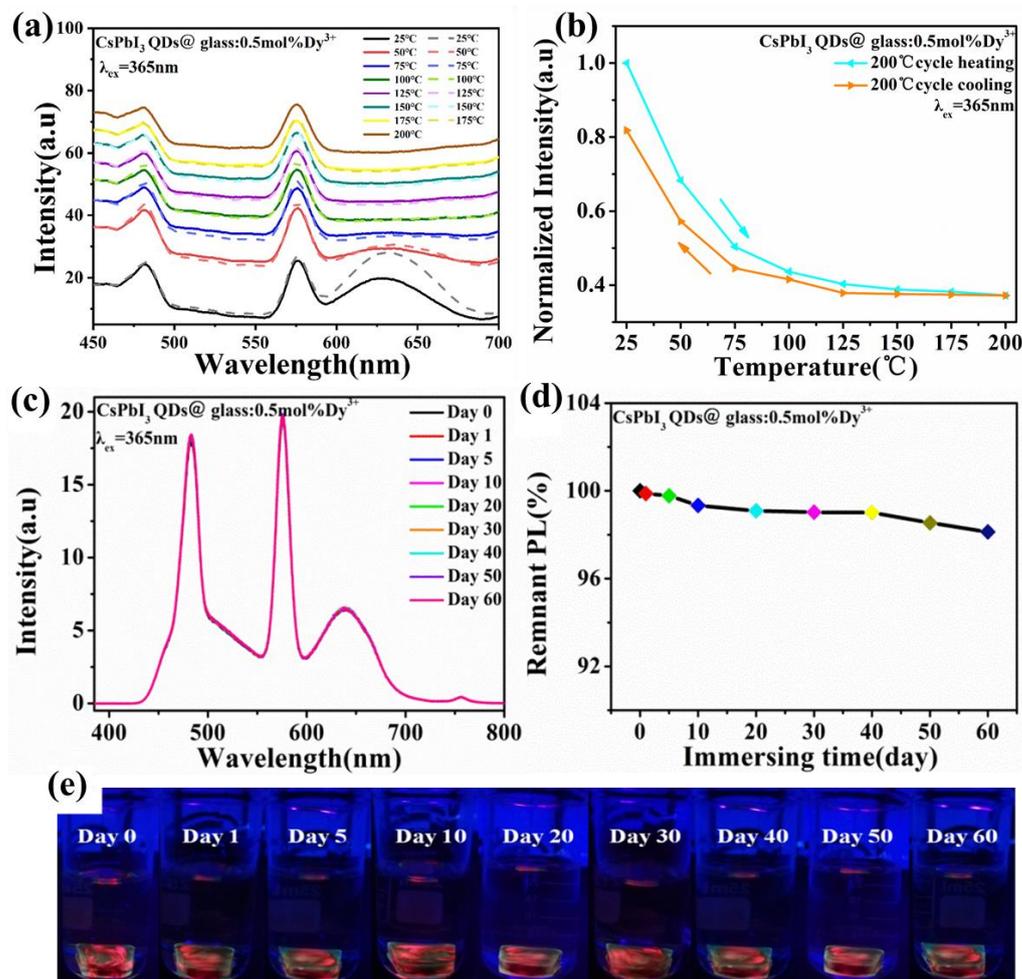


1
2 **Figure 3.** (a) Absorption spectra of CsPbI₃ QDs glasses doped with different concentrations
3 of Dy³⁺. The illustration shows the amplified absorption spectra near 690 nm (b) Emission
4 spectra of glass samples excited by ultraviolet light at 365 nm. (c) The corresponding
5 absolute quantum yield of CsPbI₃ PQDs glass doped with different concentrations of Dy³⁺
6 under excitation at 365 nm. Inset: the RIR value of CsPbI₃ QDs glasses doped with different
7 concentrations of Dy³⁺. (d) Fluorescence attenuation curves of monitored wavelengths at
8 620-650 nm under excitation at 365 nm.

9 3.3 Thermal and moisture stabilities

10 Poor stability is a major problem which limits the use of CsPbI₃ quantum dots in
11 different applications^[32]. The samples were tested for stability and Figure 4a presents
12 the temperature-dependent PL spectra of glass sample measured at an excitation of
13 365 nm. It can be seen that there is no obvious change of the two characteristic peaks
14 of Dy³⁺ with the temperature rise to 200 from 25°C, but the emission intensity of
15 CsPbI₃ PQDs decreases continuously, which is due to the non-radiative transition and
16 lattice relaxation of the luminescence center. Interestingly, as shown in Figure 4b, the
17 intensity of luminescence recovered gradually until it was 82% of its initial intensity
18 as temperature dropped. In addition, the moisture resistance test results showed that
19 the location and intensity of emission peaks of glass sample had little change after 60
20 days (Figure 4c) The integral intensity of PL peak only decreased by less than 5%
21 (Figure 4d), and luminance and color also was no significant change (Figure 4e).
22 Similarly, PLQY is measured as 9.82% for day 0 and 9.79% for day 60 revealing very

1 close values. Therefore, it can be concluded that an inorganic glass host is indeed
 2 beneficial to efficiently protect PQDs from decomposition by water. In summary, it is
 3 borosilicate zinc glass matrix that improves remarkably the thermal stability and
 4 moisture resistance of Dy³⁺ doped CsPbI₃ PQDs.



5
6

7 **Figure 4.** (a) CsPbI₃: temperature-dependent fluorescence spectra of Dy³⁺ perovskite quantum
 8 dot glass in the range of 25-200°C under excitation at 365 nm; (b) CsPbI₃: Heating and cooling
 9 cycle of emission strength of Dy³⁺ perovskite quantum dot glass from 25°C to 200°C; (c) PL
 10 spectrum of Dy³⁺ doped CsPbI₃ perovskite quantum dot glass irradiated by UV lamp at 365 nm
 11 during immersion in water for 60 days; (d) The variation of the integral intensity of peak PL
 12 with time; (e) Photoluminescence photos of Dy³⁺ doped CsPbI₃ perovskite quantum dot glass
 13 under the irradiation of 365 nm UV lamp during immersion in water for 60 days

14 3.4. CIE chromaticity coordinates and light-emitting devices

15 Due to the excellent optical properties and stability of the prepared Dy-doped CsPbI₃
 16 PQDs@glasses, we consider it may have potential application in W-LEDs^[33]. It is
 17 well known that the most common way to produce W-LEDs is to combine a
 18 yellow-emitting yttrium aluminum garnet phosphor with a blue-emitting LED chip^[34].

1 This is inconvenient for the human eye to recognize the original color of the object
2 due to its lack of a red-emitting portion^[35]. In this work, we prepared Dy-doped
3 CsPbI₃ PQDs@glasses, which can be used as a supplement to red light emission. A
4 series of fluorescent glass films of CsPbI₃ PQDs with different dysprosium
5 concentrations are prepared. The prepared glass samples of Dy³⁺ doped CsPbI₃
6 quantum dots were ground into powders and dispersed in a uniform mixture of
7 solvents which is terpineol and ethyl cellulose ten to one in a certain proportion
8 prepared a non-precipitating and uniform fluorescent slurry. Subsequently, the
9 fluorescent paste was then evenly applied to the round glass substrate by a rotary
10 coating method. Ultimately, the fluorescent glass film was prepared by drying the
11 organic matter to completely volatilize for 3 hours in a draught drying cabinet at 150°C
12 (Figure. 5a). As shown in Figure 5b, it is can be seen the color of the glass film
13 gradually changes under UV light. Noteworthy, when the doping concentration of
14 Dy³⁺ is 0.5 mol%, the color of the glass changes into yellowish-white, manifesting
15 that the as-prepared samples can be applied to W-LED. Therefore, the as-prepared
16 Dy-doped CsPbI₃ PQDs@glass was combined with a UV chip to construct a W-LED
17 device (Figure. 5c). Then the photoelectric properties of the LED devices were
18 measured at a current of 20 mA. Besides, the color of these light-emitting diodes
19 changes from red to yellow-green, and it can be certified in the CIE color coordinate
20 diagram (Figure. 5d). The locus of CsPbI₃:0.5 mol% Dy³⁺ glass sample were in a
21 blackbody radiance curve emitting dazzling white light. The corresponding CIE
22 coordinates (x, y), correlated color temperature (CCT), color rendering index (CRI)
23 and purity are listed in Table 1. Therefore, by modifying the content of Dy in the
24 CsPbI₃ PQDs glass sample, the optical parameter can be easily tuned to find the best
25 W-LED. The excellent performance of the W-LED device indicates that the
26 as-prepared CsPbI₃ PQDs glass has potential applications in solid-state lighting and
27 display^[36].

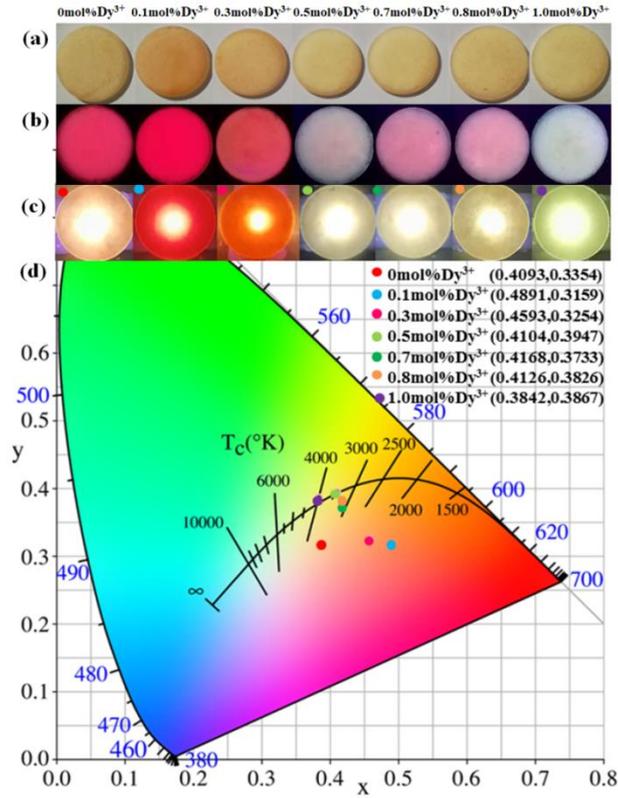


Figure 5. (a) CsPbI₃ PQDs fluorescent glass films with different Dy³⁺ doping concentrations;(b) a photograph of it under an ultraviolet lamp;(c) Light emitting photos of the prepared white LED devices;(d) CIE color coordinates

Table 1 Optical performance devices of white LED devices with different Dy³⁺ concentrations

Dy ₂ O ₃ Concentration (mol%)	CIE coordinates	CCT (K)	CRI	Purity (%)
0	(0.4093,0.3354)	2874	52.9	23.4
0.1	(0.4891,0.3159)	1676	29.3	41.5
0.3	(0.4593,0.3254)	2015	6.6	35.4
0.5	(0.4104,0.3947)	3423	86.6	41.6
0.7	(0.4168,0.3733)	3104	89.7	37.1
0.8	(0.4126,0.3826)	3273	95.6	38.7
1.0	(0.3842,0.3867)	3974	69.7	31.4

4. Conclusion

In summary, Dy³⁺-doped borosilicate glasses embedding CsPbI₃ PQDs were successfully prepared by a conventional melt quenching method, and the effect of Dy on optical properties of CsPbI₃ quantum dots has been investigated systematically. The TEM measurements verified that Dy³⁺ doped CsPbI₃ quantum dots are uniformly distributed in the glass. Since the increase of Dy³⁺ doping, the average size of CsPbI₃

1 PQDs is reduced, leading to blue shift of absorption cut-off wavelength and emission
2 peak. The element distribution diagram shows that a part of Dy^{3+} exists the lattice of
3 $CsPbI_3$ quantum dots, which promotes the formation of $CsPbI_3$ QDs. The effect of
4 excessive Dy doping is opposite. The fluorescence spectrum revealed that the doping
5 concentration circa 0.1 mol% is conducive to the generation of quantum dots, and the
6 maximum quantum efficiency of 31.8% is obtained. Most importantly, benefiting
7 from the remarkable optical performance and thermal stability, a simple W-LED was
8 fabricated by combining UV chips based on the remote Dy^{3+} doped $CsPbI_3$ PQDs
9 glass film, which demonstrated outstanding CRI of 95.6 at an operating current of 20
10 mA. By modifying the content of Dy in the $CsPbI_3$ PQDs glass sample, the color of
11 simple W-LED can be easily modified without the other photoluminescent material
12 system. This work exploits a new strategy to prepare high-performance $CsPbI_3$ PQDs
13 glass and provides an interesting insight to develop their practical applications in solid
14 state lighting and display.

15

16 **Acknowledgement**

17 Yongzheng Fang acknowledges financial supported by the the National Key Research
18 and Development Program of China (Grant No. 2021YFB3500500). Guoying Zhao
19 acknowledges financial supported by Science and Technology Talents Development
20 Fund for Young Middle-aged Teachers Fund, Collaborative Innovation Fund (No.
21 XTCX2022-03) of Shanghai Institute of Technology and Development of key
22 technologies for the preparation and application of high-performance rare earth
23 fluorescent block materials (No. BFXT-2022-D0046).

24

25 **References:**

- 26 [1] Qi F, Shao X, Ma Y, et al. Improved luminescent performances of $CsPbI_3$ perovskite quantum
27 dots via optimizing the proportion of boron-silicate glass and precipitation processing[J]. *Optical*
28 *Materials*, 2022, 124: 111981.
- 29 [2] Huang X, Guo Q, Yang D, et al. Reversible 3D laser printing of perovskite quantum dots inside
30 a transparent medium[J]. *Nature Photonics*, 2020, 14(2): 82-88.
- 31 [3] Lin J, Lu Y, Li X, et al. Perovskite Quantum Dots Glasses Based Backlit Displays[J]. *ACS*
32 *Energy Letters*, 2021, 6(2): 519-528.
- 33 [4] Peng Q, Wang T, Tang H, et al. Up- Converted Long Persistent Luminescence from $CsPbBr_3$
34 Nanocrystals in Glass[J]. *Laser & Photonics Reviews*, 2022: 2200449.
- 35 [5] Kim Y, Yassitepe E, Voznyy O, et al. Efficient luminescence from perovskite quantum dot
36 solids[J]. *ACS applied materials & interfaces*, 2015, 7(45): 25007-25013.

- 1 [6] Liao M, Shan B, Li M. In situ Raman spectroscopic studies of thermal stability of all-inorganic
2 cesium lead halide (CsPbX_3 , X= Cl, Br, I) perovskite nanocrystals[J]. The journal of physical
3 chemistry letters, 2019, 10(6): 1217-1225.
- 4 [7] Ye Y, Zhang W, Zhao Z, et al. Highly luminescent cesium lead halide perovskite nanocrystals
5 stabilized in glasses for light- emitting applications[J]. Advanced Optical Materials, 2019, 7(9):
6 1801663.
- 7 [8] Yuan R, Shen L, Shen C, et al. CsPbBr_3 : xEu^{3+} perovskite QD borosilicate glass: a new
8 member of the luminescent material family[J]. Chemical communications, 2018, 54(27):
9 3395-3398.
- 10 [9] Chen D, Yuan S, Chen X, et al. CsPbX_3 (X= Br, I) perovskite quantum dot embedded
11 low-melting phosphosilicate glasses: controllable crystallization, thermal stability and tunable
12 emissions[J]. Journal of Materials Chemistry C, 2018, 6(25): 6832-6839.
- 13 [10] Ai B, Liu C, Wang J, et al. Precipitation and optical properties of CsPbBr_3 quantum dots in
14 phosphate glasses[J]. Journal of the American Ceramic Society, 2016, 99(9): 2875-2877.
- 15 [11] Li X, Yu Y, Hong J, et al. Optical temperature sensing of Eu^{3+} -doped oxyhalide glasses
16 containing CsPbBr_3 perovskite quantum dots[J]. Journal of Luminescence, 2020, 219: 116897.
- 17 [12] Chen D, Yuan S, Chen J, et al. Robust CsPbX_3 (X = Cl, Br, and I) perovskite quantum dot
18 embedded glasses: nanocrystallization, improved stability and visible full-spectral tunable
19 emissions[J]. Journal of Materials Chemistry C, 2018.
- 20 [13] Chen D, Liu Y, Yang C, et al. Promoting photoluminescence quantum yields of
21 glass-stabilized CsPbX_3 (X = Cl, Br, I) perovskite quantum dots through fluorine doping[J].
22 Nanoscale, 2019, 11(37): 17216-17221.
- 23 [14] Liu S, Luo Y, He M, et al. Novel CsPbI_3 QDs glass with chemical stability and optical
24 properties[J]. J Eur Ceram Soc, 2018, 38(4): 1998-2004.
- 25 [15] Kibrish O, Erol E, Ersundu M Ç, et al. Robust CsPbBr_3 and CdSe/Dy^{3+} CdSe quantum dot
26 doped glass nanocomposite hybrid coupling as color converter for solid-state lighting
27 applications[J]. Chemical Engineering Journal, 2021, 420: 130542.
- 28 [16] Wang Z, Shen X, Tang C, et al. Efficient and Stable CF_3PEAI -Passivated CsPbI_3 QDs toward
29 Red LEDs[J]. ACS Applied Materials & Interfaces, 2022, 14(6): 8235-8242.
- 30 [17] Xie B, Hu R, Luo X. Quantum dots-converted light-emitting diodes packaging for lighting
31 and display: status and perspectives[J]. Journal of Electronic Packaging, 2016, 138(2): 020803.
- 32 [18] Erol E, Kibrish O, Ersundu M Ç, et al. Color tunable emission from Eu^{3+} and Tm^{3+} co-doped
33 CsPbBr_3 quantum dot glass nanocomposites[J]. Physical Chemistry Chemical Physics, 2022,
34 24(3): 1486-1495.
- 35 [19] Zekri M, Herrmann A, Turki R, et al. Experimental and theoretical studies of Dy^{3+} doped
36 alkaline earth aluminosilicate glasses[J]. Journal of Luminescence, 2019, 212: 354-360.
- 37 [20] Ma Y, Zhao G, Guo Y, et al. Structural characterization and photoluminescence properties of
38 B_2O_3 - Bi_2O_3 - SiO_2 glass containing Dy^{3+} ions[J]. Journal of Luminescence, 2020, 227: 117591.
- 39 [21] Kim J S, Eswaran S K, Kwon O H, et al. Enhanced Luminescence Characteristics of Remote
40 Yellow Silicate Phosphors Printed on Nanoscale Surface-Roughened Glass Substrates for White
41 Light-Emitting Diodes[J]. Advanced Optical Materials, 2016, 4(7): 1081-1087.
- 42 [22] Erol E, Vahedigharehchopogh N, Ekim U, et al. Ultra-stable $\text{Eu}^{3+}/\text{Dy}^{3+}$ co-doped CsPbBr_3
43 quantum dot glass nanocomposites with tunable luminescence properties for phosphor-free WLED
44 applications[J]. Journal of Alloys and Compounds, 2022, 909: 164650.

- 1 [23] Zheng R, Ueda J, Shinozaki K, et al. In Situ Growth Mechanism of CsPbX₃ (X= Cl, Br, and I)
2 Quantum Dots in an Amorphous Oxide Matrix[J]. Chemistry of Materials, 2022, 34(4):
3 1599-1610.
- 4 [24] Zhao G, Xu L, Meng S, et al. Facile preparation of plasmon enhanced near-infrared
5 photoluminescence of Er³⁺-doped Bi₂O₃-B₂O₃-SiO₂ glass for optical fiber amplifier[J]. J Lumin,
6 2019, 206: 164-168.
- 7 [25] Reza Dousti M, Sahar M R, Rohani M S, et al. Nano-silver enhanced luminescence of
8 Eu³⁺-doped lead tellurite glass[J]. J Mol Struct, 2014, 1065-1066: 39-42.
- 9 [26] Dousti M R, Poirier G Y, Amjad R J, et al. Luminescence quenching versus enhancement in
10 WO₃-NaPO₃ glasses doped with trivalent rare earth ions and containing silver nanoparticles[J].
11 Opt Mater, 2016, 60: 331-340.
- 12 [27] Zhu Y, Yang B, Lu Q, et al. Stable Dy-doped CsPbBr₃ quantum dot glass with enhanced
13 optical performance[J]. Journal of Non-Crystalline Solids, 2022, 575: 121224.
- 14 [28] Li P, Duan Y, Lu Y, et al. Nanocrystalline structure control and tunable luminescence
15 mechanism of Eu-doped CsPbBr₃ quantum dot glass for WLEDs[J]. Nanoscale, 2020, 12(12):
16 6630-6636.
- 17 [29] Lu C, Li H, Kolodziejski K, et al. Enhanced stabilization of inorganic cesium lead triiodide
18 (CsPbI₃) perovskite quantum dots with tri-octylphosphine[J]. Nano Research, 2018, 11(2):
19 762-768.
- 20 [30] Shamshad L, Rooh G, Kirdsiri K, et al. Photoluminescence and white light generation
21 behavior of lithium gadolinium silicoborate glasses[J]. Journal of Alloys and Compounds, 2017,
22 695: 2347-2355.
- 23 [31] Uma V, Maheshvaran K, Marimuthu K, et al. Structural and optical investigations on Dy³⁺
24 doped lithium tellurofluoroborate glasses for white light applications[J]. Journal of Luminescence,
25 2016, 176: 15-24.
- 26 [32] Erol E, Kıbrıslı O, Ersundu M Ç, et al. Size-controlled emission of long-time durable
27 CsPbBr₃ perovskite quantum dots embedded tellurite glass nanocomposites[J]. Chemical
28 Engineering Journal, 2020, 401: 126053.
- 29 [33] Yuan L, Zhou L, Xiang W, et al. Enhanced stability of red-emitting CsPbI₃: Yb³⁺ nanocrystal
30 glasses: A potential luminescent material[J]. Journal of Non-Crystalline Solids, 2020, 545:
31 120232.
- 32 [34] Chen H-S, Hsu C-K, Hong H-Y. Ingan-cdse-znse quantum dots white LEDs[J]. Ieee
33 photonics technology letters, 2005, 18(1): 193-195.
- 34 [35] Xuan T-T, Liu J-Q, Xie R-J, et al. Microwave-assisted synthesis of CdS/ZnS: Cu quantum
35 dots for white light-emitting diodes with high color rendition[J]. Chemistry of Materials, 2015,
36 27(4): 1187-1193.
- 37 [36] Jiang J, Shao G, Zhang Z, et al. Ultrastability and color-tunability of CsPb (Br/I)₃
38 nanocrystals in P-Si-Zn glass for white LEDs[J]. Chemical Communications, 2018, 54(87):
39 12302-12305.
- 40

CRedit authorship contribution statement

Chaotong Zhou: Conceptualization, Writing-original draft. **Yu Ma:** Data curation, Formal analysis. **Fan Jiang:** Methodology, Investigation. **Guoying Zhao:** Methodology, Investigation, Supervision. **Jingshan Hou:** Methodology, Investigation. **Yufeng Liu:** Methodology, Validation. **Xin Qiao:** Investigation, Writing - Review & Editing. **Zhongzhi Wang:** Resources. **Ji-Guang Li:** Funding acquisition. **Yongzheng Fang:** Supervision.

Declaration of interests

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.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: