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ORIGINAL PAPERS

Electron beam-induced white emission from iridium complexes-doped polymer dots

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Abstract

Radiation detection plays an important role in diverse applications, including medical imaging, security, and display technologies. Scintillators, materials that emit light upon exposure to radiation, have garnered significant attention due to their exceptional sensitivity. Previous research explored polymer dots (P-dots) doped with iridium complexes as nano-sized scintillators for radiation detection, but these were constrained to emitting specific colors like red, green, and blue, limiting their utility. Recently, there has been a breakthrough in the development of white light emitters stimulated by UV–visible light. These emitters exhibit a broad spectral range in the visible wavelength, enhancing contrast and simplifying detection by visible-light sensors. Consequently, the quest for white color scintillators in radiation detection has emerged as a promising avenue for enhancing scintillation efficiency. In this study, we present a novel approach by applying P-dots doped with two iridium complexes to create white light-emitting nano-sized scintillators. These scintillators offer a wider spectral coverage within the visible-light wavelength range. Under UV light (365 nm) excitation, our synthesized P-dots exhibited remarkable white light emission. Moreover, when excited by electron beam irradiation, we observed the clear emission close to white emission which is valuable for improving the detection of radiation.

Keywords Nanomaterials · Scintillation · Luminescence · Polymer dots

1 Introduction

Radiation detection is crucial for various applications, including medical imaging, security, and display [1, 2]. Scintillators, materials that emit light when exposed to radiation, have been widely employed in radiation detection because of their high sensitivity [3–6]. In a previous work, we studied function of polymer dots (P-dots) doped with iridium complex as nano-sized scintillators for radiation detection [7–9]. These scintillators, however, have been restricted to specific colors such as red, green, and blue, limiting their emission wavelength range.

Recently, white light emitters excited by UV–visible light have been reported for use in imaging and organic light-emitting diodes [10–12]. These emitters exhibit broad spectral coverage in the visible wavelength range, improving contrast for easier detection by visible-light detectors [13–15]. Consequently, the development of white color scintillators for radiation detection is a promising avenue for improving scintillation efficiency [16]. These white scintillators offer wider spectral coverage and may further enhance efficiency

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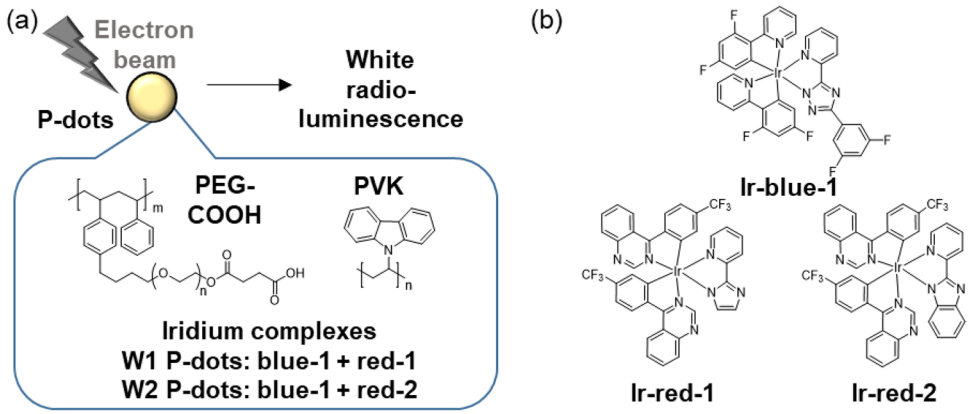

Fig. 1 **a** Schematic of P-dots in white radio-luminescence induced by electron beam irradiation. **b** Chemical structure of the iridium complex used in this study

for scintillation, potentially improving photodetectors in the radiation detection system as well. In this study, we demonstrate application of P-dots to white light-emitting nano-sized scintillators using iridium complexes, which allows a wider range of spectral coverage in the detection of visible-light wavelength range.

2 Results and discussion

2.1 Molecular design for white light-emitting P-dots by electron beam excitation

Figure 1 shows a conceptual diagram of white radio-luminescence induced by electron beam irradiation and the chemical structures of the iridium complexes used in

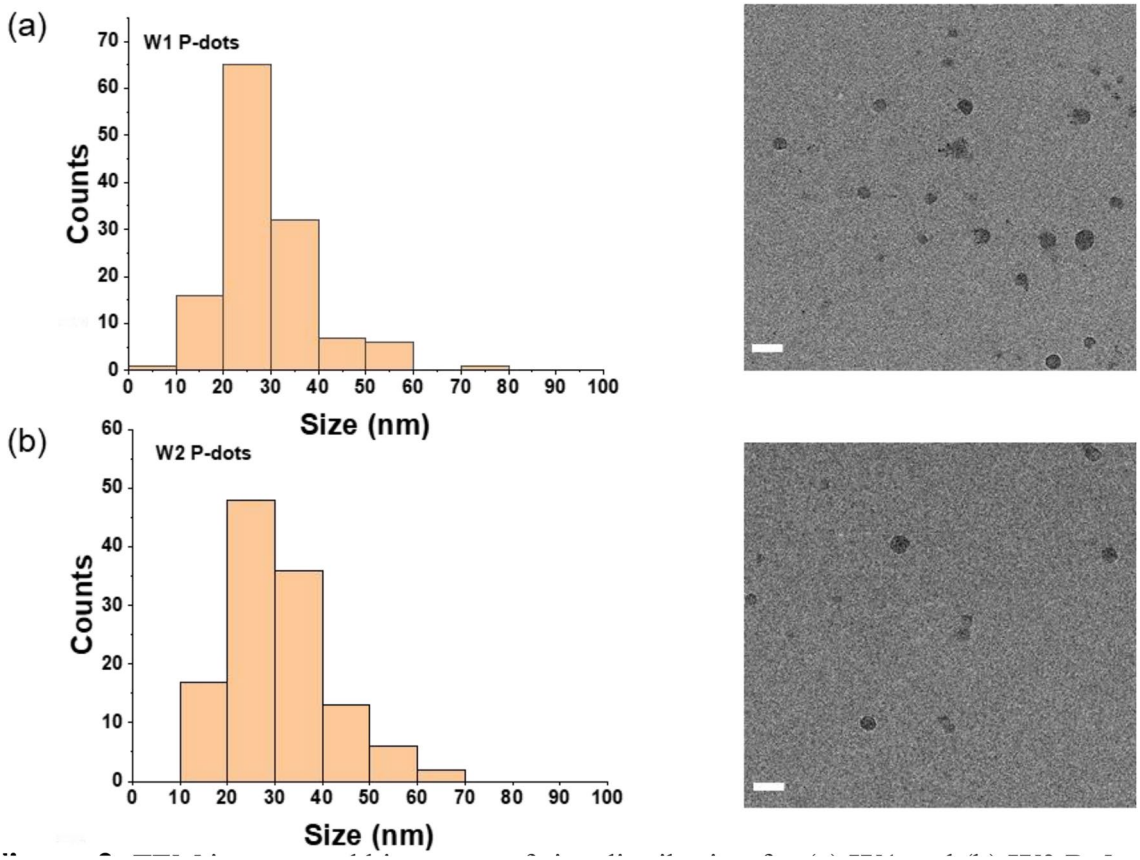

Fig. 2 TEM images and histogram of size distribution for **a** W1 and **b** W2 P-dots. Scale bar is 50 nm

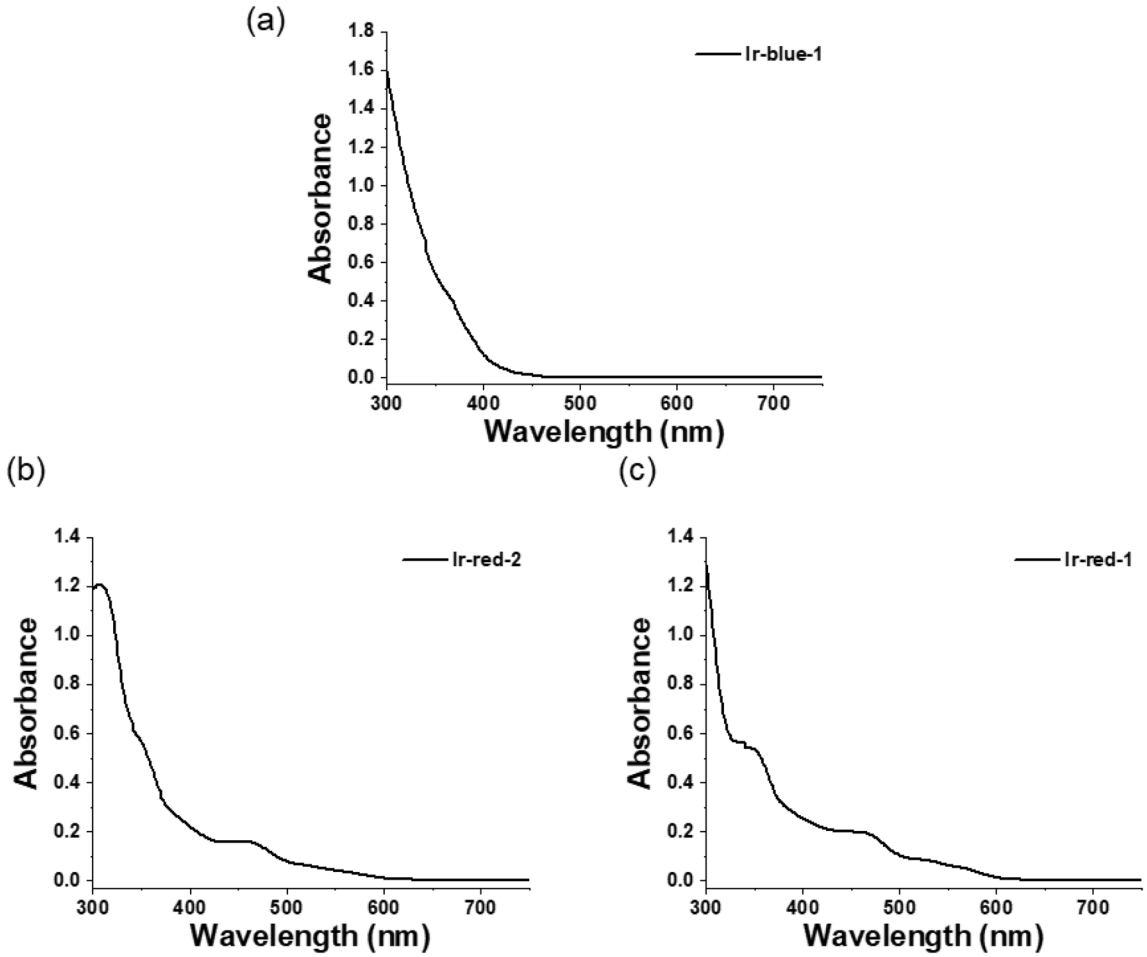

Fig. 3 The absorption spectra of **a** Ir-blue-1, **b** Ir-red-1, and **c** Ir-red-2 in acetonitrile

this study. Previously, we reported the P-dots that show radio-luminescence in red, yellow, and blue, respectively. To synthesize those showing various colors, the ligands of heteroleptic iridium complexes were designed to be P-dots, which emit light in response to X-rays and electron beam irradiation. The full width at half maximum (FWHM) of the emission band was less than 100 nm [7], and thus, the color wavelength range of the emission was limited. To achieve a broader spectral coverage, i.e., one that exhibits a wider range of emission wavelengths, especially white ones, the present study designed iridium complexes-doped P-dots that exhibit white radio-luminescence. In particular, we designed to synthesize white luminescent P-dots by co-doping blue and red luminescent iridium complexes (Fig. 1b). The synthesis scheme of each iridium complex is shown in Figs. S1–3. The synthesized iridium complexes were identified by ^{1}H-NMR and MALDI mass spectra (Figs. S4–7). White radioluminescent P-dots were synthesized by co-precipitation of the synthesized monomer iridium complexes with PEG–COOH and PVK polymers, because the amphiphilic PEG–COOH is used to synthesize water soluble nanoparticles and PVK acts as a carrier for nanoparticle formation (Table S1). To synthesize white luminescent P-dots, the concentration conditions were optimized, the best are shown here. The iridium complexes synthesized this time have low solubility in water and are almost doped into the nanoparticles. In fact, we have confirmed it by filter filtration and centrifugation that there was almost no free iridium complexes. The size of the synthesized P-dots was evaluated by TEM and DLS measurements (Fig. 2 and Table S2). The TEM images showed that the average sizes of the P-dots were around 30 nm (Table S2). The

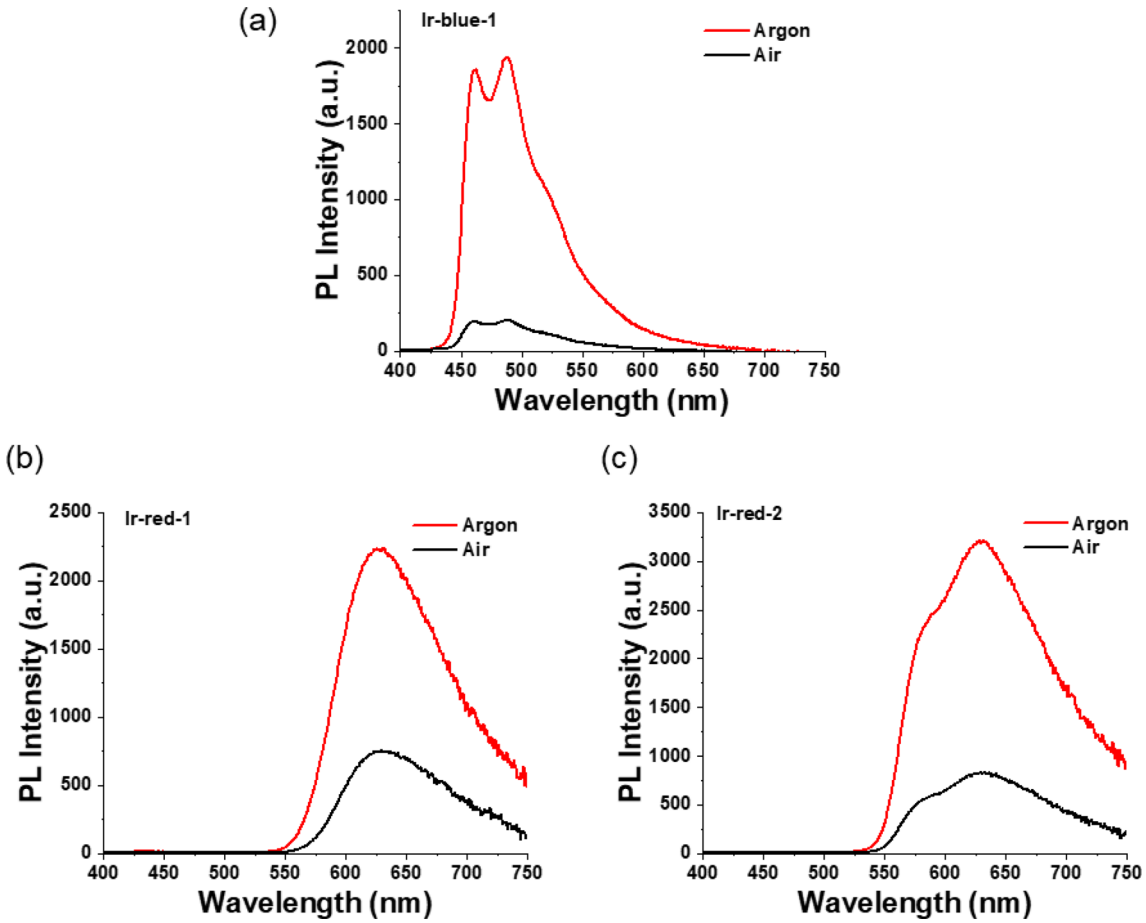

Fig. 4 The PL spectra of **a** Ir-blue-1, **b** Ir-red-1, and **c** Ir-red-2 in acetonitrile under argon (red) and air (black) conditions

Table 1 The absolute PL quantum yields (Φ) of the iridium complexes

	Φ_{argon}	Φ_{air}
Ir-blue-1	0.04	0.02
Ir-red-1	0.60	0.16
Ir-red-2	0.52	0.15

Measured with excitation at 355 nm at room temperature in toluene. Degassed with argon bubbling for 10 min

hydrodynamic diameters of the P-dots examined by DLS measurements were around 135 nm (Table S2). The zeta potentials of the P-dots were around – 25 mV, which implied the negatively charged outer surface of the P-dots due to the carboxyl groups of the amphiphilic PEG–COOH polymers (Table S2). From the measurements, it can be concluded that the P-dots co-doped with two iridium complexes were synthesized successfully. In the next sections, we report the photochemical properties of the synthesized monomeric iridium complexes themselves and P-dots.

2.2 Photochemical properties of monomeric iridium complex in organic solvents

The photochemical properties of iridium complexes in organic solvents were investigated in the first place. In the absorption spectra, the three iridium complexes in acetonitrile showed broad absorption bands in the UV and visible-light regions (300–600 nm) (Fig. 3). The photoluminescence (PL) spectra were measured in acetonitrile upon excitation at 365 nm at room temperature, as shown in Fig. 4. Ir-blue-1 displayed emission with maxima at 462 and 487 nm. Ir-red-1 exhibited emission with a maximum of 626 nm, and Ir-red-2 showed emission with a maximum of 632 nm. In the presence of O_2, we observed quenching of the PL (Fig. 4). The

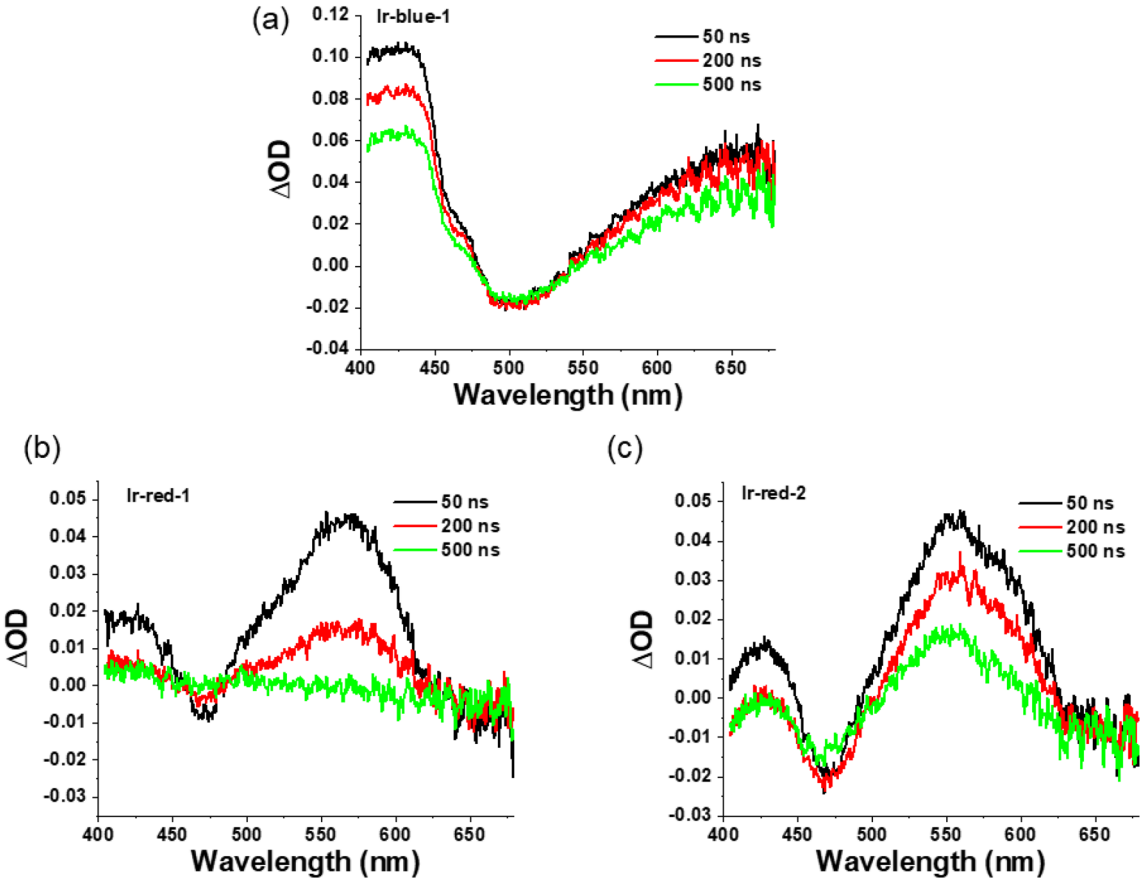

Fig. 5 Transient absorption spectra during laser flash photolysis of **a** Ir-blue-1, **b** Ir-red-1, and **c** Ir-red-2 in acetonitrile

absolute PL quantum yields of the iridium complexes were measured in toluene (Table 1).

We also observed the quenching of PL by O_2. To further study the O_2-quenching, we investigated the triplet excited states of the iridium complexes in acetonitrile by laser flash photolysis (Figs. 5 and 6). The absorption maxima of the triplet excited states were at 430, 570, and 550 nm for Ir-blue-1, Ir-red-1, and Ir-red-2, respectively. The lifetimes of the triplet excited states were measured (Fig. 6) as listed in Table 2. It was found that the rate constants of quenching (k_q) were close to the diffusion-limited rate constant in the organic solvent, implying that the triplet excited states were quenched within 1 μs (Table 2).

2.3 Photochemical properties of P-dots co-doped with two types of iridium complexes

We co-doped Ir-blue-1, and Ir-red-1 or Ir-red-2 to make white light-emitting W1 or W2 P-dots, respectively. The absorption and PL spectra of the W1 and W2 P-dots are shown in Fig. 7. In the PL spectra excited upon 365 nm, W1 P-dots displayed emission maxima in blue (455, 486 nm) and red color regions (608 nm), while W2 P-dots displayed emission maxima in blue (455, 486 nm) and red color regions (622 nm) (Fig. 7). We did not observe O_2-quenching on the PL of the P-dots (Fig. S8). The absolute PL quantum yields (H_2O) of the P-dots are shown in Table S3. As shown in Table S3, the PL quantum yields of the P-dots were independent of the presence of O_2. The PL quantum yields of P-dots were lower than that of the monomer, which was attributed to quenching due to aggregation [7, 17].

Upon UV light (365 nm) irradiation, we observed clear emission from W1 and W2 P-dots (Fig. 7). We determined the chromaticity coordinates of W1 and W2 P-dots by employing CIE 1931 color space (Fig. 7d). The chromaticity coordinates of Ir-blue-1 P-dots, Ir-red-1 P-dots, and Ir-red-2 P-dots were also shown for comparison. The (x, y) chromaticity coordinates are listed in Table S4. It was found that the W1 and W2 P-dots showed similar coordinates of (0.33, 0.33) and (0.32, 0.33), respectively, which were close

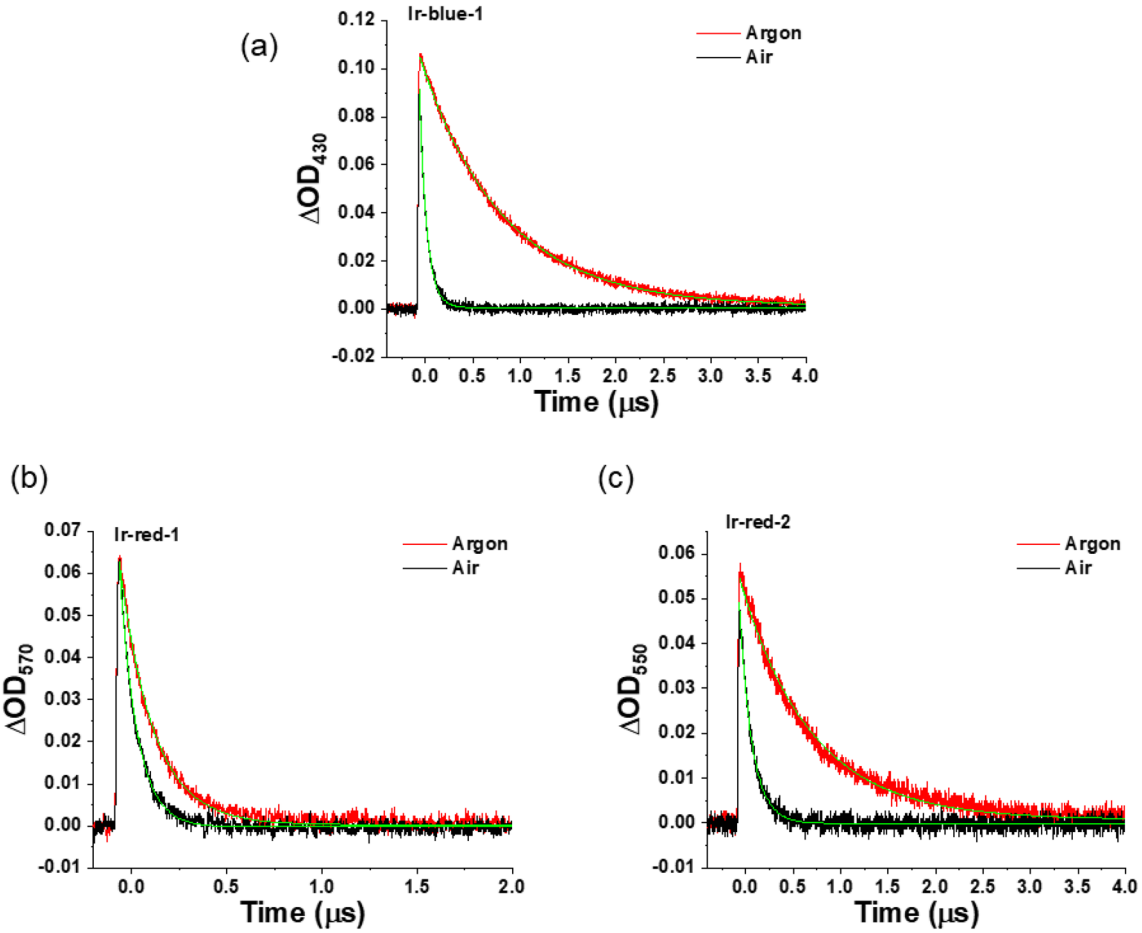

Fig. 6 Time profiles for **a** Ir-blue-1, **b** Ir-red-1, and **c** Ir-red-2 in acetonitrile under argon (red) and air (black)

Table 2 The triplet excited state lifetimes (τ) and rate constants of quenching by O_2 (k_q) of the iridium complexes

	τ_{argon} (μs)	τ_{air} (μs)	k_q (10^9 L mol^{-1} s^{-1})
Ir-blue-1	0.87	0.08	6.0
Ir-red-1	0.18	0.09	2.9
Ir-red-2	0.74	0.14	3.0

Measured with a 355 nm laser at room temperature in acetonitrile. Degassed with argon bubbling for 10 min

to white light emission (0.33, 0.33). Based on these results, we confirmed white emission from W1 and W2 P-dots under UV light (365 nm) irradiation.

2.4 Electron beam-induced luminescence of P-dots

Finally, the luminescent performance of the P-dots upon electron beam irradiation was studied. We employed an electron beam from a linear accelerator (28 MeV) for the irradiation. During the pulse radiolysis, W1 and W2 P-dots exhibited similar luminescence spectra

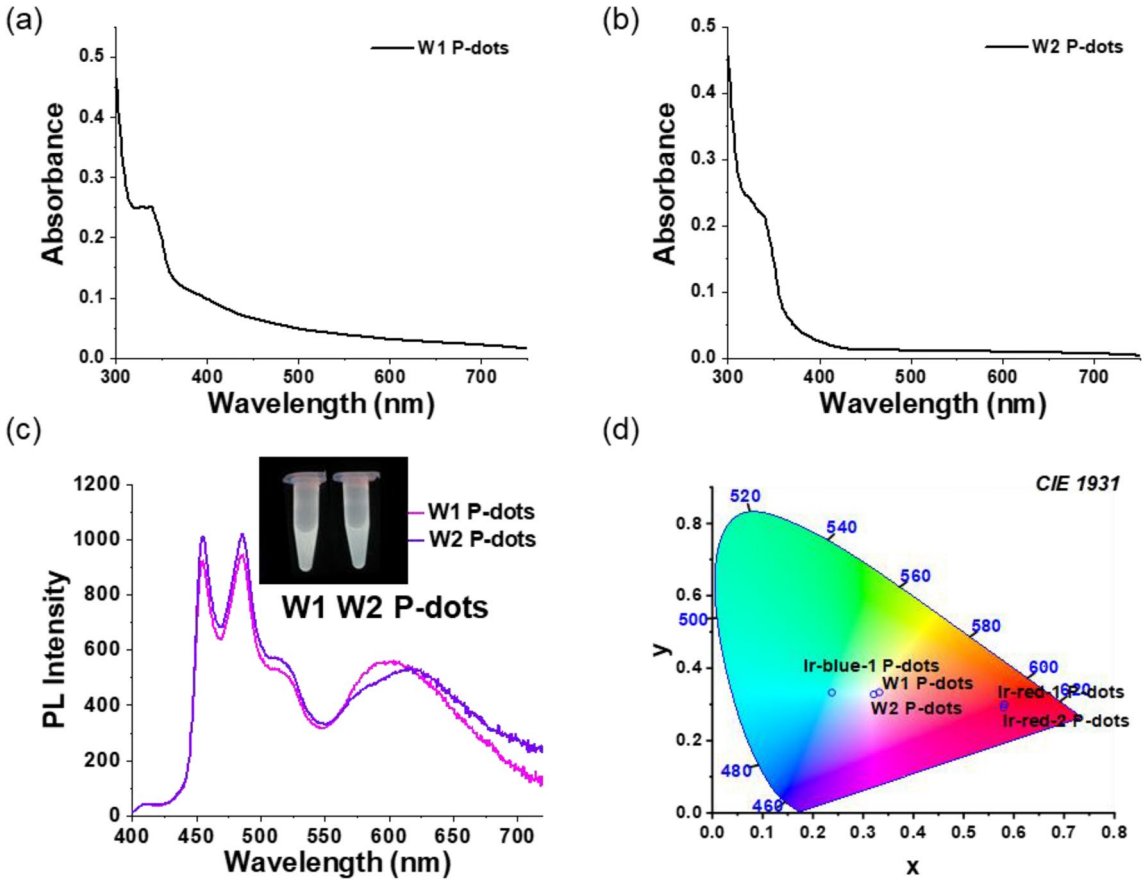

Fig. 7 The absorption spectra of **a** W1 and **b** W2 P-dots in H_2O. **c** PL spectra of W1 and W2 P-dots and photograph under UV light (365 nm) irradiation. **d** Color map of the P-dots

with emission maxima in blue region (492 nm) and in red region (589 nm) (Fig. 9). The CIE 1931 color space chromaticity diagram (Fig. 9b) revealed the coordinates of (0.42, 0.41) and (0.42, 0.41) for W1 and W2 P-dots, respectively, which were close to white light emission (0.33, 0.33) with correction with the sensitivity correction of multichannel detector (Figs. 8, 9 and Tables S5 and S6). We also observed their luminescence directly using

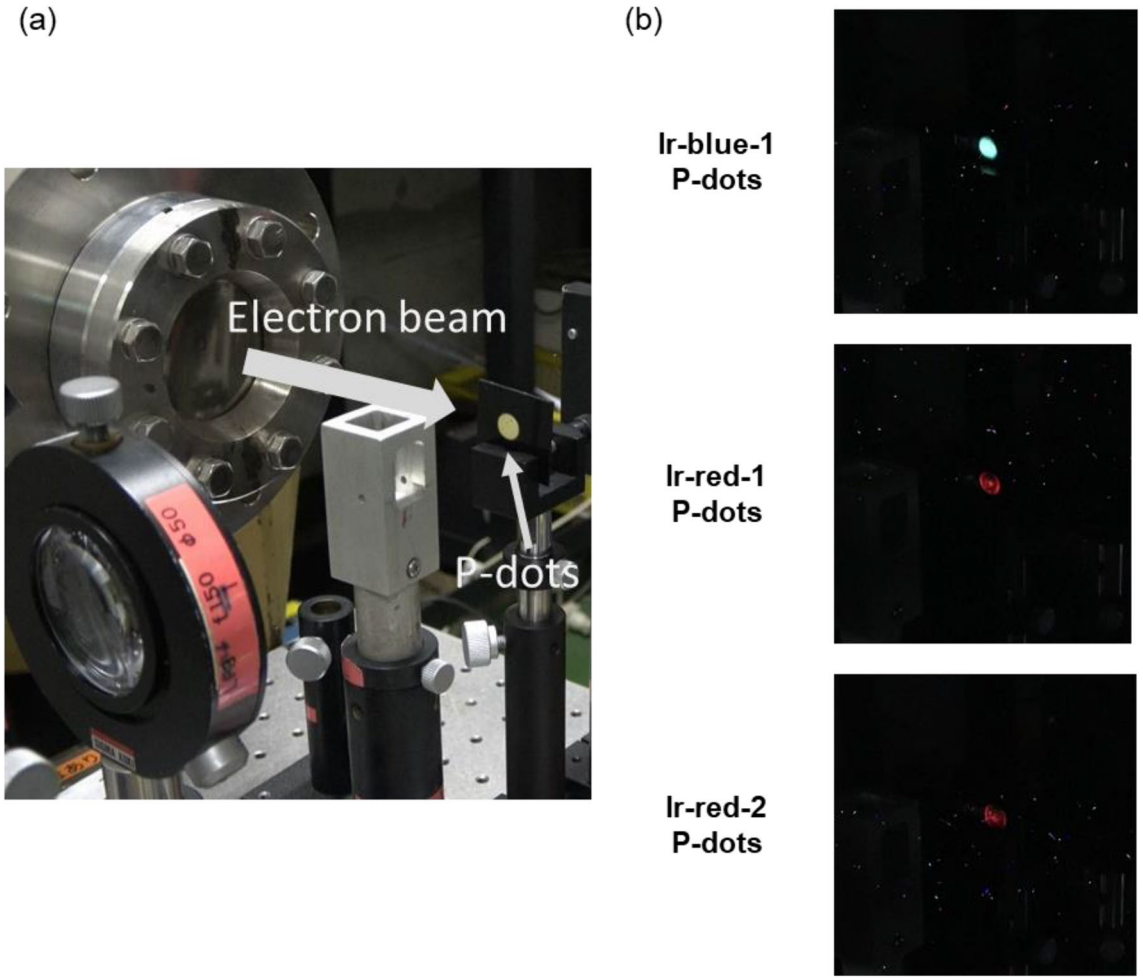

Fig. 8 **a** Photographs of an experiment using a video camera to measure luminescence. **b** The electron beam-induced luminescence images for Ir-blue-1, Ir-red-1, and Ir-red-2 P-dots

a 4 K video camera during electron beam excitation. It is essential to produce scintillator films with higher luminance using the strategy of producing uniform particles once as P-dots and then converting them into films as previously reported by us [7]. We clearly observed their white-colored emission from W1 and W2 P-dots in solid state coated on an acrylic plate, while we observed red and blue emission in Ir-blue-1 P-dots, Ir-red-1 P-dots, and Ir-red-2 P-dots, respectively. These results observed upon electron beam were in accordance with those excited under UV light (365 nm) irradiation.

3 Conclusion

In this study, P-dots co-doped with two iridium complexes were synthesized and their use for white light emission was investigated. Under UV light (365 nm) excitation, white light

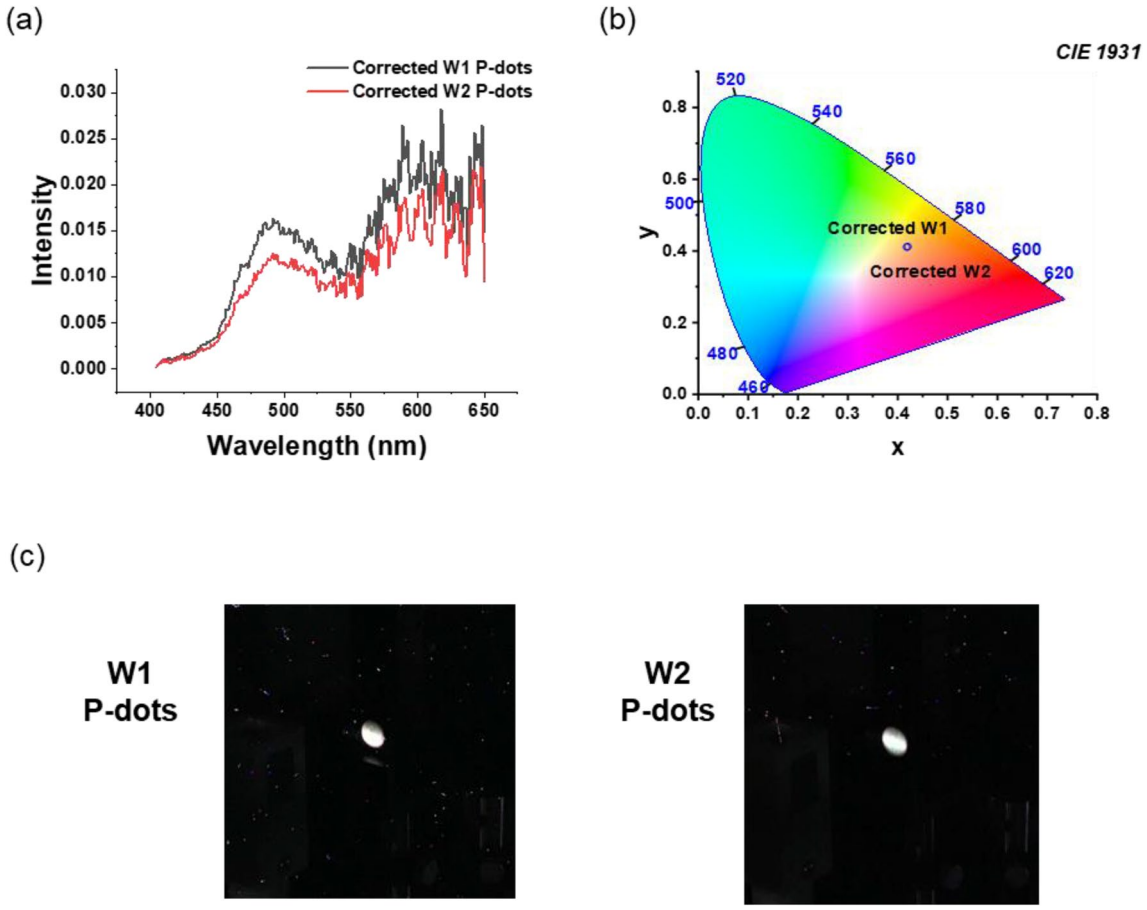

Fig. 9 **a** The electron beam-induced luminescence spectra of W1 and W2 P-dots with correction. **b** Color map of the P-dots with correction. **c** The electron beam-induced luminescence images for W1 and W2 P-dots

emission was observed from these P-dots. Upon electron beam irradiation, we observed their luminescence close to white light emission.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s43630-023-00520-3.

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Availability of data and materials The datasets used and/or analyzed during the current study are available from the corresponding authors on reasonable request.

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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