

Benzoic Acid–Polymer Composites as Radiophotoluminescent Materials for X-Ray Dosimetry

Tomoaki Yashiro

Shizuoka University

Masanori Koshimizu

`koshimizu.masanori@shizuoka.ac.jp`

Shizuoka University

Research Article

Keywords:

Posted Date: August 25th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10647222/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Benzoic Acid–Polymer Composites as Radiophotoluminescent Materials for X-Ray Dosimetry

*Tomoaki Yashiro¹, Masanori Koshimizu^{2*}

¹ Department of Electronic Material Science, Shizuoka University, 3-5-1 Johoku, Chuo-ku, Hamamatsu 432-8011, Japan

² Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Chuo-ku, Hamamatsu, 432-8011, Japan

Corresponding author: koshimizu.masanori@shizuoka.ac.jp

Abstract

Solid-state radiophotoluminescence (RPL) dosimeters based on organic materials were developed. Focusing on the generation of fluorescent molecules from the reaction between benzoic acid in polymers and radicals, samples of PMMA, PVC, and PVA containing benzoic acid at different concentrations were prepared. The responses of these samples were evaluated by measuring the photoluminescence spectra before and after X-ray irradiation. In the PVA samples before and after X-ray irradiation, the emission peak was observed at 412 nm and is attributed to salicylic acid. The photoluminescence intensity increased upon X-ray irradiation. Based on the FT-IR spectra of the samples, the increase in the photoluminescence intensity after X-ray irradiation is attributed to the formation of salicylic acid. At the optimal benzoic acid concentration of 1 wt%, the linear response range was 0–60 Gy. In the PMMA samples before and after X-ray irradiation, the emission peak was observed at 435 nm and is attributed to benzoic acid tetramers. The photoluminescence intensity increased upon X-ray irradiation. Based on the FT-IR spectra of the samples, the increase in the photoluminescence intensity is attributed to an increase in the photoluminescence efficiency of benzoic acid tetramers resulting from PMMA oxidation. At the optimal benzoic acid concentration of 1 wt%, the linear response range was 0–100 Gy. In the PVC samples before and after X-ray irradiation, the emission peak was observed at 437 nm and is attributed to benzoic acid tetramers. The

photoluminescence intensity decreased upon X-ray irradiation. Based on the FT-IR spectra of the samples, the decrease in the photoluminescence intensity is attributed to the decomposition of benzoic acid tetramers. The radiation-induced reactions in the PMMA and PVA samples can potentially be utilized as the operating principle for organic RPL dosimeters.

1. Introduction

Radiation therapy is one of the primary treatments for cancer. Ionizing radiation can destroy cancer cells or cause genetic changes resulting in cancer cell death [1]. Since it does not require surgical resection of the tumor, radiation therapy is an effective treatment that places less strain on the body. Radiation therapy includes external beam radiation therapy [2], in which radiation is delivered from outside the body; brachytherapy [3], in which radioactive sources are inserted into the body; and nuclear medicine therapy [4], in which radioactive substances are administered orally or via injection. In external beam radiation therapy, technological advances—achievement of complex dose distribution using multi-leaf collimators and precise control of the beam characteristics using modern accelerators—enable the focused high dose to the tumor while minimizing the radiation dose to normal tissues. In intensity-modulated radiation therapy, the radiation beam intensity is modulated according to the arrangement of the target and surrounding organs [5]. In image-guided radiation therapy, volumetric imaging performed during treatment enables precise radiation delivery to the tumor itself or to the organ in which the tumor is located [6]. Consequently, there has been a growing demand in recent years for accurate measurement of radiation dose distribution.

Currently, ionization chambers and semiconductor detectors are widely used as active detectors for dose measurement in radiation therapy [7]. An ionization chamber is a device that collects ion–electron pairs generated by radiation within a cavity filled with gas as electrical charge. Due to their excellent stability, high linearity with respect to absorbed dose, and low directional dependence, they are widely used for reference dose measurements in megavolt X-ray therapy [8]. Semiconductor detectors are able to achieve excellent spatial resolution because of their high sensitivity and small sensitive volumes. However, there is an issue of poor signal-to-noise ratio at low dose rate [9]. In addition, radiochromic films and silver halide films are used as passive detectors. Radiochromic films achieve high tissue equivalence and excellent spatial resolution using organic materials and are widely used in current radiation therapy for measuring two-dimensional dose distributions. For example, GafChromic radiochromic films produce colored images when exposed to radiation with strong absorbance in the

red spectrum (575–675 nm) [10]. Silver halide films absorb radiation and form electron-hole pairs, and the electrons combine with silver ions at defect sites within the crystal to produce neutral silver atoms. As a result, silver atoms accumulate and absorb visible light, thereby creating a latent image [11]. Since many of these dosimeters used in radiation therapy are composed of materials with effective atomic numbers and radiation absorption characteristics that differ from those of biological tissue, discrepancies may arise between the measured dose distribution and the actual one within the human body [12]. For this reason, there is a need to develop tissue-equivalent dosimeters.

Several luminescence phenomena are used for dose measurements, including thermoluminescence (TL) [13], optically stimulated luminescence (OSL) [14], and radiophotoluminescence (RPL) [15]. TL and OSL are phenomena used for quantifying dose from radiation by utilizing electrons trapped in the materials. Upon stimulation by heat or light, these electrons can escape their traps and recombine with holes, exhibiting luminescence with its intensity reflecting the absorbed radiation dose. Materials used in TL dosimeters include LiF:Mg,Ti [13] and LiF:Mg,Cu,P [16], while materials used in OSL dosimeters include Al₂O₃:C [14] and BeO [17]. In radiation therapy, LiF:Mg,Cu,P chips have been put into practical use as TL dosimeters for in vivo dose measurement [18]. Furthermore, a lithium borate-based material with an effective atomic number of approximately 7.3 has been developed as a tissue-equivalent TL dosimeter [17]. RPL dosimeters have attracted attention in recent years due to their superior characteristics—high radiation sensitivity, stability, and minimal fading—compared to TL and OSL dosimeters. RPL is a phenomenon in which ionizing radiation generates new luminescent centers. The intensity of luminescence of the luminescent centers reflects the absorbed radiation dose. For example, silver-doped phosphate glass has been used as a personal dosimeter [19]. In the field of radiation therapy, it is also used for phantom dosimetry and in vivo dosimetry [20]. However, most RPL dosimeters are composed of inorganic materials with high effective atomic numbers. Thereby, there is a need for the development of tissue-equivalent RPL dosimeters.

In previous studies, an aqueous RPL dosimeter using benzoic acid was developed [21]. Upon X-ray irradiation, hydroxyl radicals are generated in the aqueous solution and react with benzoic acid to

produce salicylic acid, causing an increase in the photoluminescence intensity. Based on a similar principle, aqueous solution dosimeters using terephthalic acid, trimesic acid, and coumarin-3-carboxylic acid have also been developed [22,23,24]. In addition, water-based organic gel dosimeters using benzoic acid have been developed. By using nanoclay, the dosimeters have high sensitivity in the 1–5 Gy range [25]. Furthermore, nanoclay gel dosimeters containing terephthalic acid, trimesic acid, and coumarin-3-carboxylic acid have been developed [25,26]. RPL dosimeters based on aqueous solutions and nanoclay gels possess sufficient sensitivity for dose measurement in radiation therapy. However, the measured dose distribution becomes blurred due to the diffusion of the active chemical species within the matrix and a decrease in sensitivity at high temperatures [27,28].

Solid-state organic RPL dosimeters have been developed based on polymers and dye molecules. Upon exposure to X-rays, the dosimeters are endowed with fluorescent properties. A PVC-based dosimeter containing coumarin-3-carboxylic acid exhibited a linear response in the 100–500 Gy range when exposed to X-rays ($\text{CuK}\alpha$) from an X-ray generator with a dose rate of 500 Gy min^{-1} [29]. In addition, a PVC-based dosimeter using 2',7'-dichlorofluorescein diacetate was developed and exhibited a linear response over a dose range of 100–4,000 Gy [30]. As a solid-state dosimeter that combines high sensitivity with tissue equivalence, a dosimeter combining BQ and fluorescein in a PMMA–propylene carbonate host has been reported [31]. This dosimeter exhibited a linear response in the 2–4 Gy range. However, there are few reports of highly sensitive materials among polymer-based solid dosimeters, and there is a need to develop sensitive solid-state RPL dosimeters. Although sensitization using inorganic phosphors has also been attempted, the inclusion of inorganic phosphors adversely affects the tissue equivalence of the dosimeter [32].

In this study, we focused on the generation of fluorescent molecules such as salicylic acid resulting from the reaction between benzoic acid in polymers and radicals. Polymethyl methacrylate (PMMA), polyvinyl chloride (PVC), and polyvinyl alcohol (PVA) were selected as polymers for dispersing benzoic acid. PMMA is a polymer with excellent transparency and processability, while PVC has a

high radiation chemical yield of radical generation [33]. PVA contains hydroxyl groups and is expected to efficiently generate hydroxyl radicals upon X-ray irradiation [34]. We prepared samples of PMMA, PVC, and PVA containing benzoic acid at various concentrations. The responses of these materials were evaluated by acquiring the photoluminescence spectra before and after X-ray irradiation.

2. Experiments

PMMA, PVC, and PVA were used as the host polymers. Benzoic acid, PMMA, PVC, PVA, and tetrahydrofuran (THF) were purchased from Fujifilm Wako Pure Chemical. The raw materials were used as received without further purification.

Three kinds of materials were fabricated by adding benzoic acid to PMMA, PVC, or PVA. The PMMA and PVC samples were prepared as follows. PMMA or PVC (5.0 g) was dissolved in 50 ml of THF in beakers. The solutions were then divided into plastic (PFA) beakers so that each beaker contained 0.5 g of PMMA or PVC. Benzoic acid (0.5 g) was dissolved in 50 ml of THF, and the resulting solution was added to the polymer solution. The PVA samples were prepared as follows. PVA (2.5 g) was dissolved in 50 ml of distilled water in a beaker. The solution was then divided into PFA beakers so that each beaker contained 0.5 g of PVA. Benzoic acid (0.5 g) was dissolved in distilled water, and the resulting solution was added to the PVA solution. The concentrations of benzoic acid were 0.3, 0.6, 1, 3, 6, or 10 wt% with respect to the host polymers. The solutions were dried for longer than 7 d in the dark. The solid samples were peeled off the surface of the beaker.

The samples were irradiated with X-rays at a dose rate of 1 Gy/min using an X-ray generator (Spellman XRB80N100) operated at a tube voltage of 80 kV and a tube current of 1.2 mA. The photoluminescence spectra were acquired using a spectrofluorometer (Shimazu RF-5300PC) equipped with a xenon lamp. The FT-IR spectra were measured using a Fourier transform infrared spectrophotometer (JASCO FT/IR-6300) with the attenuated total reflection (ATR) method.

3. Results and Discussion

Fig. 1(a) and (b) show the photographs of the PMMA samples containing 1 wt% benzoic acid before and after X-ray irradiation at 100 Gy, respectively. Similarly, Fig. 1(c) and (d) show the photographs of the PVC samples containing 1 wt% benzoic acid, and Fig. 1(e) and (f) show those of the PVA samples containing 1 wt% benzoic acid before and after X-ray irradiation at 100 Gy, respectively. All the samples were colorless and transparent with no coloration due to the X-ray or the excitation light irradiation.

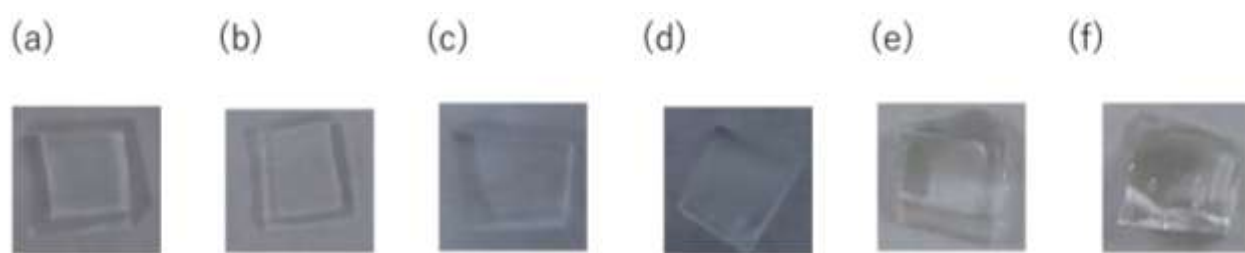


Fig. 1 (a) Photographs of PMMA containing 1 wt% benzoic acid before and (b) after X-ray irradiation at 100 Gy, (c) Photographs of PVC containing 1 wt% benzoic acid before and (d) after X-ray irradiation at 100 Gy, (e) Photographs of PVA containing 1 wt% benzoic acid before and (f) after X-ray irradiation at 100 Gy.

Fig. 2(a) shows the excitation spectra of the PVA sample containing 1 wt% benzoic acid before and after X-ray irradiation at 100 Gy. The emission wavelength was 412 nm. Since the excitation peak wavelength is similar to that of salicylic acid dissolved in water, it is attributed to salicylic acid [35]. The peak wavelength of the excitation spectra did not change, and its intensity increased after X-ray irradiation. Salicylic acid was also generated in an aqueous solution of benzoic acid: the photoluminescence and excitation spectra of the aqueous solution of benzoic acid, longer than one day after dissolution, were similar to those of the PVA samples. Fig. S1 shows the excitation and photoluminescence spectra of an aqueous solution of benzoic acid stored in the dark and under room lighting for a week. The peak wavelengths of the excitation and photoluminescence spectra of the aqueous solution stored under room lighting were 297 nm and 417 nm, respectively, and the peak wavelengths of the excitation spectrum and photoluminescence spectrum of the aqueous solution stored in the dark were 294 nm and 413 nm, respectively. The peak wavelengths were similar to those

of the PVA sample. The aqueous solution stored under room lighting showed higher intensities in both the excitation and photoluminescence spectra than those stored in the dark, indicating that room light promoted salicylic acid production. Because the aqueous solution of benzoic acid was not completely protected from light in my experiment, salicylic acid was produced through a photooxidation reaction [36]. In addition, the benzoic acid reagent used in this study contained trace amounts of iron impurities (less than 5 ppm), which may have acted as catalysts for the photooxidation reaction. Fig. 2(b) shows the photoluminescence spectra of the PVA samples containing 1 wt% benzoic acid. The excitation wavelength was set to the excitation peak wavelength of 300 nm. The photoluminescence peak was observed at 412 nm and is attributed to salicylic acid [35]. The photoluminescence intensity at 412 nm increased with increasing dose from 0 to 100 Gy. This result indicates that salicylic acid was generated upon X-ray irradiation.

Fig. 2(c) shows the peak intensities at 412 nm of the photoluminescence spectra of the PVA samples containing benzoic acid at different concentrations at different X-ray doses. The shapes of the photoluminescence spectra for all the samples were similar to that shown in Fig. 2(b). The intensity on the vertical axis is normalized to the photoluminescence peak intensity of each sample before irradiation. The normalized intensity of the sample with 1 wt% benzoic acid increased linearly with dose from 0 to 60 Gy. This result indicates the achievement of RPL and suggests that salicylic acid was generated upon X-ray irradiation. During the measurements of the photoluminescence spectra in the range of 0–100 Gy, the samples were irradiated with the excitation light for approximately 2 min. The photoluminescence intensity of the 1 wt% benzoic acid sample decreased by 8.5% with the excitation light irradiation at 300 nm for 2 min. Since the photoluminescence intensity increased by 14.0% after 100 Gy of irradiation, the increase in the photoluminescence intensity of the PVA samples is due to X-ray irradiation and not to the irradiation of the excitation light. As the benzoic acid concentration increased from 0.3 wt% to 1 wt%, the slope of the normalized photoluminescence intensity with respect to dose became larger in the range of 0–60 Gy. This is attributed to an increase in the number of benzoic acid molecules involved in the reaction, resulting in higher salicylic acid

production yield per unit dose. As the concentration increased from 1 wt% to 10 wt%, the slope of the normalized photoluminescence intensity with respect to irradiation dose became smaller in the range of 0–60 Gy. This is because the increase in benzoic acid caused an increase in the salicylic acid in the samples before X-ray irradiation, which reduces the increase in the normalized photoluminescence intensity by X-ray irradiation. These results indicate that the optimal benzoic acid concentration in the PVA sample for X-ray responsivity was 1 wt%.

The photoluminescence intensities of the 0.6 and 1 wt% samples increased more gradually with X-ray irradiation from 60 to 100 Gy compared to the range of 0–60 Gy. This result indicates that the rate of salicylic acid degradation increased relative to the amount of salicylic acid produced by irradiation.

The photoluminescence intensities of the 0.3, 3, 6, and 10 wt% samples decreased by at least 13.0% with X-ray irradiation from 80 to 100 Gy, which exceeds the intensity reduction caused by the excitation light, indicating that the X-ray irradiation caused the decomposition of salicylic acid at high dose.

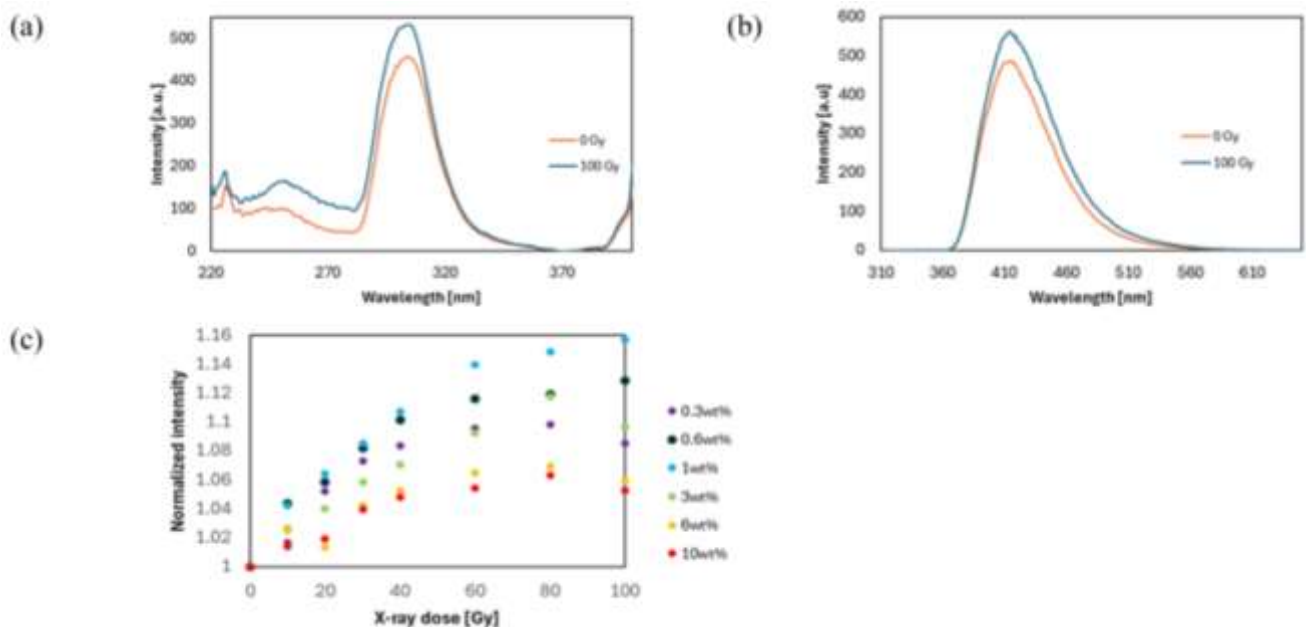


Fig. 2. (a) Photoluminescence excitation and (b) emission spectra of PVA containing 1 wt% benzoic acid before and after X-ray irradiation. (c) Peak intensities in photoluminescence spectra of the PVA

samples containing benzoic acid at different concentrations at different X-ray doses

Fig. 3(a) shows the excitation spectra of the PMMA sample containing 1 wt% benzoic acid before and after X-ray irradiation at 100 Gy. The emission wavelength was 435 nm. The excitation peaks were observed at 380 and 396 nm. When the PMMA sample containing 1 wt% benzoic acid was irradiated with X-rays, the peak wavelengths of the excitation spectra did not change, and its intensity at 380 nm increased. Fig. 3(b) shows the photoluminescence spectra of the PMMA samples containing 1 wt% benzoic acid. Because the maximum excitation peak was observed at 380 nm, the excitation wavelength was set to the excitation peak wavelength of 380 nm. The photoluminescence peaks were observed at 410 nm and 435 nm with a shoulder peak at 460 nm. Upon irradiation with X-rays, the peak wavelengths of the photoluminescence spectra did not change, and the intensities at 410 nm and 435 nm, as well as the intensity of a shoulder peak at 460 nm, increased. These excitation and emission wavelengths differ from the literature values for both benzoic acid [37] and salicylic acid [35].

We discuss the origin of the excitation peaks observed in the PMMA samples. Fig. S2 shows the excitation spectrum of the THF solution of benzoic acid (0.01 g/ml), longer than one day after dissolution. The excitation peak was observed at 379 nm, which is consistent with the 380-nm peak observed in the PMMA sample. From this result, the molecules corresponding to the excitation peaks observed in the PMMA samples were formed in the THF solution. Fig. S3 shows the excitation spectrum of the toluene solution of benzoic acid (0.01 g/ml), longer than one day after dissolution. The excitation peaks were observed at 306 nm and 376 nm. The latter peak indicates that the toluene solution contains the same molecules as the PMMA sample and the THF solution. Although benzoic acid is a common component in all the samples and solutions, benzoic acid monomers are non-fluorescent molecules, and benzoic acid dimers have an excitation wavelength at 285 nm, which is shorter than the observed excitation wavelength [37]. Therefore, the excitation peak at 380 nm observed in the PMMA samples cannot be attributed to benzoic acid monomers or dimers. Next, we discuss the origin of the photoluminescence emission peaks observed in the PMMA samples. Fig. S2

shows the photoluminescence spectrum of a THF solution of benzoic acid (0.01 g/ml), longer than one day after dissolution. The photoluminescence peaks were observed at 409 nm and 430 nm with a shoulder peak at 457 nm, which are consistent with those observed in the PMMA sample. Fig. S3 shows the photoluminescence spectrum of a toluene solution of benzoic acid (0.01 g/ml), longer than one day after the dissolution. The photoluminescence peaks were observed at 414 nm and 437 nm with a shoulder peak at 461 nm, which are consistent with those observed in the PMMA sample and the THF solution. From these results, the molecules corresponding to the photoluminescence peaks observed in the PMMA samples were formed in the THF and toluene solutions. Although benzoic acid is a common component in all the samples and solutions, benzoic acid monomers are non-fluorescent molecules, and benzoic acid dimers have an emission wavelength at 310 nm, which is shorter than the observed photoluminescence wavelength [37]. Benzoic acid can form higher-order aggregates larger than dimers in toluene. In a previous study, FT-IR spectroscopy and NMR chemical shift measurements have shown that benzoic acid forms dimers through hydrogen bonding and tetramers through π - π stacking in toluene. The proportion of the tetramers resulting from π - π stacking is less than a few percent compared to hydrogen-bonded dimers [38]. The association of benzoic acid tetramers by π - π stacking can also be observed in other aromatic molecules. For example, a face-to-face dimer of sym-triphenylcycloheptatriene is known to form a relaxed excited state and exhibit a significant red shift in its photoluminescence spectrum compared to the monomer [39]. Face-to-face π -stacking of anthracene also caused a significant redshift in the photoluminescence wavelength of up to 150 nm [40]. Similarly to these examples, it is expected that the excitation and photoluminescence wavelengths of benzoic acid tetramers exhibit a redshift in both spectra compared to those of benzoic acid dimers. Hence, the common excitation and photoluminescence peaks observed in the PMMA sample, THF solution, and toluene solution are attributed to the benzoic acid tetramers. The origin of the 306-nm excitation peak observed in the toluene solution could not be determined.

Fig. 3(c) shows the peak intensities at 435 nm of the photoluminescence spectra of the PMMA samples

containing benzoic acid at different concentrations at different X-ray doses. The shapes of the photoluminescence spectra for all the samples were similar to those shown in Fig. 3(b). The intensity on the vertical axis is normalized to the intensity of each sample before irradiation. The normalized intensity of the sample with 1 wt% benzoic acid increased linearly with dose from 0 to 100 Gy. This result indicates the achievement of RPL, and that new fluorescent molecules were generated or the luminescence efficiency of existing molecules was enhanced upon irradiation. The photoluminescence intensities of the 0.6, 3, 6, and 10 wt% samples increased more gradually with X-ray irradiation from 60 to 100 Gy compared to the range of 0–60 Gy. The photoluminescence intensities of the 0.3 wt% samples decreased with X-ray irradiation from 40 to 100 Gy, falling by 1.5%. This result indicates that fluorescent molecules are decomposed upon X-ray irradiation.

During the measurements of the photoluminescence spectra in the range of 0–100 Gy, the samples were irradiated with the excitation light for approximately 2 min. The photoluminescence intensity of the 1 wt% benzoic acid sample increased by 2.1 % with 2-min irradiation of the excitation light at 380 nm. Since the photoluminescence intensity increased by 21.0 % after 100 Gy of irradiation, the increase in photoluminescence intensity of the PMMA sample is mainly due to X-ray irradiation

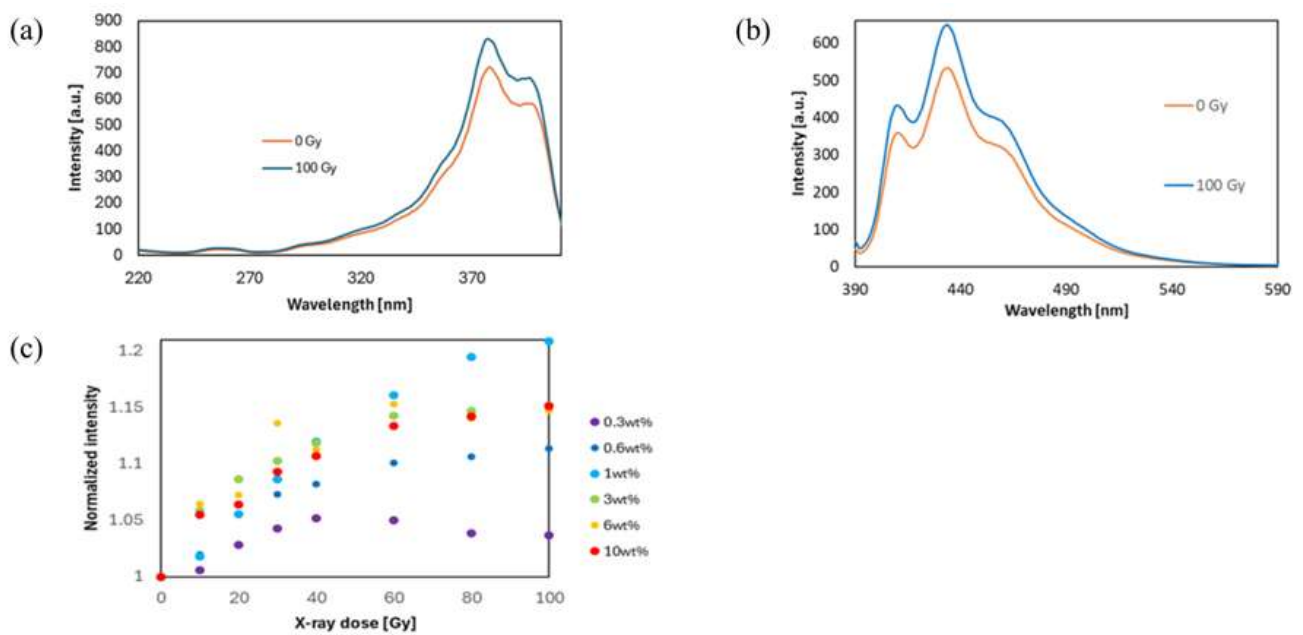


Fig. 3 (a) Photoluminescence excitation and (b) emission spectra of PMMA containing 1 wt% benzoic acid before and after X-ray irradiation, (c) Peak intensities in photoluminescence spectra of PMMA samples containing benzoic acid at different concentrations at different X-ray doses.

Fig. 4(a) shows the excitation spectra of the PVC sample containing 1 wt% benzoic acid before and after X-ray irradiation at 100 Gy. The emission wavelength was 437 nm. The excitation peaks were observed at 363 nm, 377nm, and 401 nm. The peak wavelength of the excitation spectra did not change, and its intensity decreased after X-ray irradiation. Fig. 4(b) shows the photoluminescence spectra of the PVC samples containing 1 wt% benzoic acid. Because the maximum excitation peak was observed at 377 nm, the excitation wavelength was set to the excitation peak wavelength of 377 nm. The photoluminescence peaks were observed at 414 nm and 437 nm with a shoulder peak at 463 nm. The photoluminescence intensities at 414 nm and 437 nm decreased after X-ray irradiation. The excitation and photoluminescence peaks in the PVC samples are consistent with those observed in the PMMA sample. The origin of the excitation and photoluminescence peaks in the PVC samples is identified as the benzoic acid tetramer, for the same reasons as in the case of the PMMA samples.

Fig. 4(c) shows the peak intensities at 437 nm of the photoluminescence spectra of the PVC samples containing benzoic acid at different concentrations at different X-ray doses. The shapes of the photoluminescence spectra for all the samples were similar to those shown in Fig. 4(b). The intensity on the vertical axis is normalized to the intensity of each sample before irradiation. The normalized intensities of all the samples decreased with dose from 0 to 100 Gy. Although the decrease in normalized photoluminescence intensity varied with benzoic acid concentration, no systematic concentration dependence was observed.

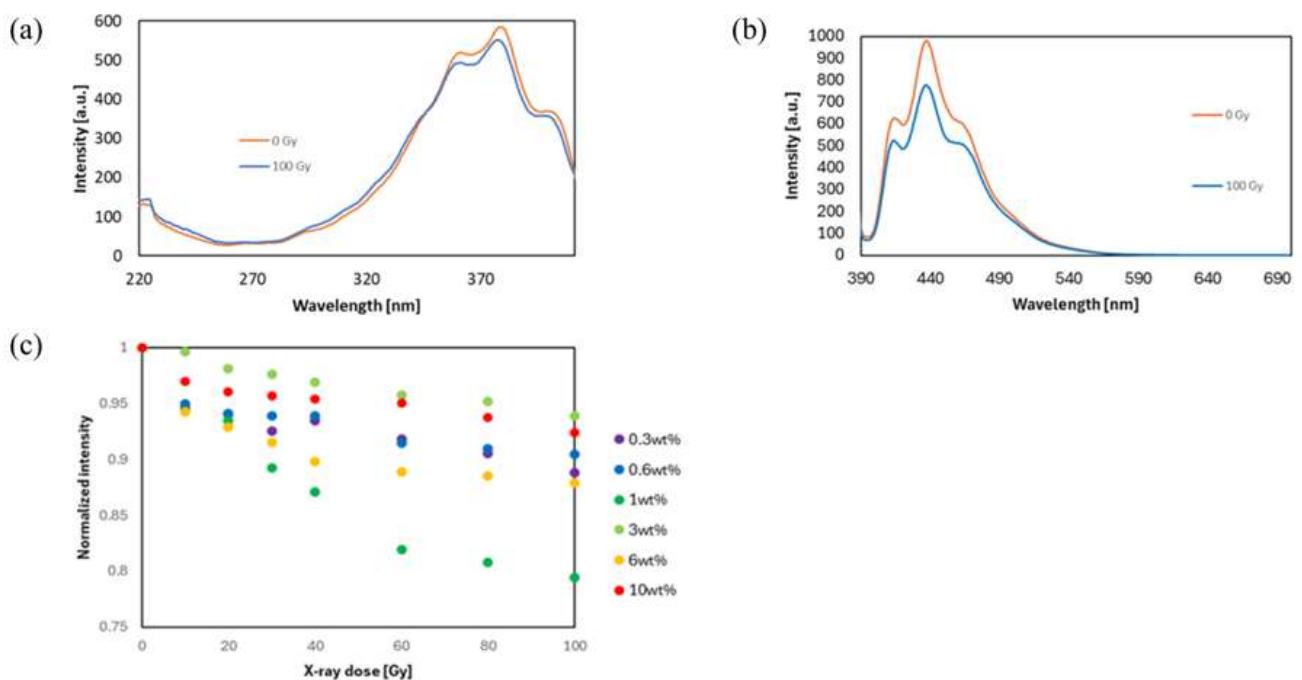


Fig. 4 (a) Photoluminescence excitation and (b) emission spectra of PVC containing 1 wt% benzoic acid before and after X-ray irradiation, (c) Peak intensities in photoluminescence spectra of the PVC samples containing benzoic acid at different concentrations at different X-ray doses.

Fig. 5(a) shows the FTIR spectra of the PVA containing 1 wt% benzoic acid before and after 100-Gy irradiation, and Fig. 5(b) shows the difference spectra. We focused on the three peaks attributed to (A) C–O stretching vibration, (B) C=O stretching vibration, and (C) O–H stretching vibration in Fig. 5(b). The peak intensities of the C–O stretching vibration (1240 cm^{-1}) and the C=O stretching vibration (1734 cm^{-1}) increased after X-ray irradiation. The broad peak of the O–H vibration shows both an

increase (3100 cm^{-1}) and a decrease (3500 cm^{-1}), which indicates that the peak position of the O-H stretching vibration has shifted toward the low wavenumber side. A previous study has shown that irradiation of PVA reduces the number of hydroxyl groups (FTIR peak at 3340 cm^{-1}) and generates hydroxyl radicals and hydrogen radicals within PVA. Hydrogen radicals react with oxygen to form hydroperoxyl radicals, which then react with PVA to form hydroxyl groups. When two hydroxyl groups bonded to the same carbon atom react, a carbonyl group and a water molecule are formed [41,42]. Therefore, the increase in the peak intensity of the C=O stretching vibration indicates that carbonyl groups were formed as a result of the reactions described above. Salicylic acid is known to have a broad O-H vibration peak at 3248 cm^{-1} and a sharp peak at 3585 cm^{-1} in its FTIR spectrum. The sharp band is assigned to the O-H stretching vibration in the carboxylic group. This peak could not be detected in the FT-IR spectra in this study, possibly owing to the superposition of the broad peak of the O-H vibration. The broad one is attributed to the phenolic OH hydrogen-bonded to the neighboring carboxyl group within the molecule [34]. Therefore, the increases in the peak intensities of the C-O stretching vibration and the low-wavenumber shift of the O-H vibration peak indicate the addition of a hydroxyl group to benzoic acid. These results indicate that hydroxyl radicals generated from PVA reacted with benzoic acid to form molecules such as salicylic acid. Based on the FTIR results, the increase in photoluminescence intensity upon X-ray irradiation is attributed to the formation of salicylic acid.

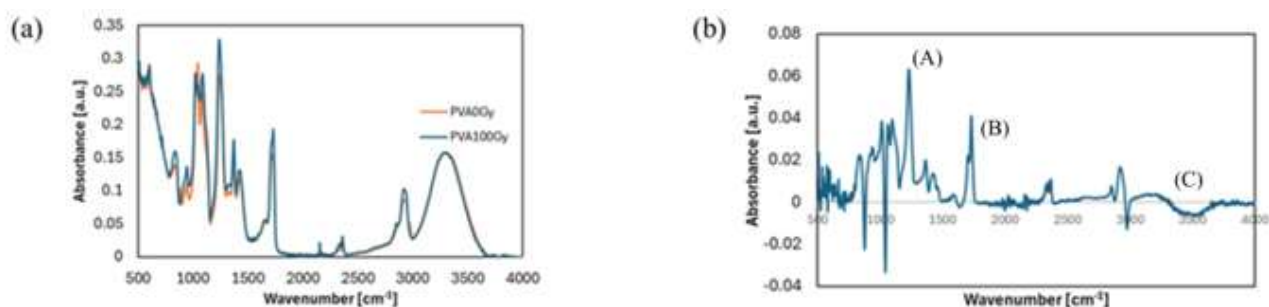


Fig. 5 (a) FTIR spectra of PVA containing 1 wt% benzoic acid before and after 100 Gy irradiation and (b) difference FTIR spectrum. (A) C-O stretching vibration, (B) C=O stretching vibration, (C) O-H stretching vibration.

Fig. 6(a) shows the FTIR spectra of PMMA containing 1 wt% benzoic acid before and after 100-Gy irradiation, and Fig. 6(b) shows the difference spectra. The peak intensities of the (A) C–O stretching vibration (1140 cm^{-1}) and (B) C=O stretching vibration (1734 cm^{-1}) increased after X-ray irradiation, which suggests that the hydroxylation of benzoic acid or the oxidation of PMMA occurred. Previous studies have shown that irradiating PMMA with gamma rays cleaves the C-H bond, generates hydrogen radicals and carbon-centered polymer radicals on the polymer chains, and the polymer radicals react with oxygen to form carbonyl groups [43]. The peak wavelengths in the excitation (Fig.3(a)) and photoluminescence (Fig.3(b)) spectra did not change upon X-ray irradiation, and a significant increase in the intensity of O–H stretching vibration peak was not observed. Therefore, it is unlikely that new molecules like salicylic acid were formed. Instead, these results indicate that the oxidation of PMMA restricted the molecular motion and suppressed non-radiative relaxation, thereby improving the photoluminescence efficiency of the benzoic acid tetramers.

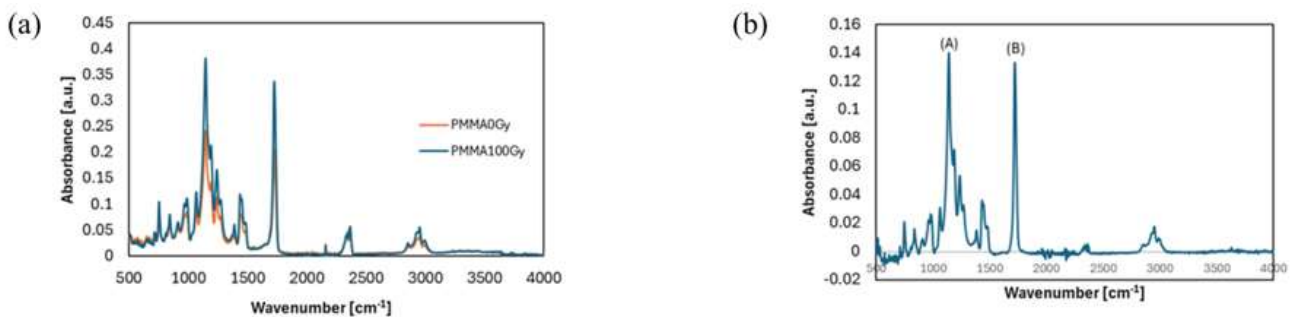


Fig. 6. (a) FTIR spectra of PMMA containing 1 wt% benzoic acid before and after 100-Gy irradiation and (b) difference FTIR spectrum. (A) C–O stretching vibration, (B) C=O stretching vibration.

Fig. 7(a) shows the FTIR spectra of PVC containing 1 wt% benzoic acid before and after 100-Gy irradiation, and Fig. 5(b) shows the difference spectrum. The peak intensities of the (A) C–Cl stretching vibration (611 cm^{-1}), (B) C–O stretching vibration (1250 cm^{-1}) and (C) C=O stretching vibration (1713 cm^{-1}) decreased after X-ray irradiation, which indicates that PVC and carboxy groups of benzoic acid were decomposed. Therefore, the decrease in photoluminescence intensity upon X-ray irradiation was due to the reduction in benzoic acid tetramer.

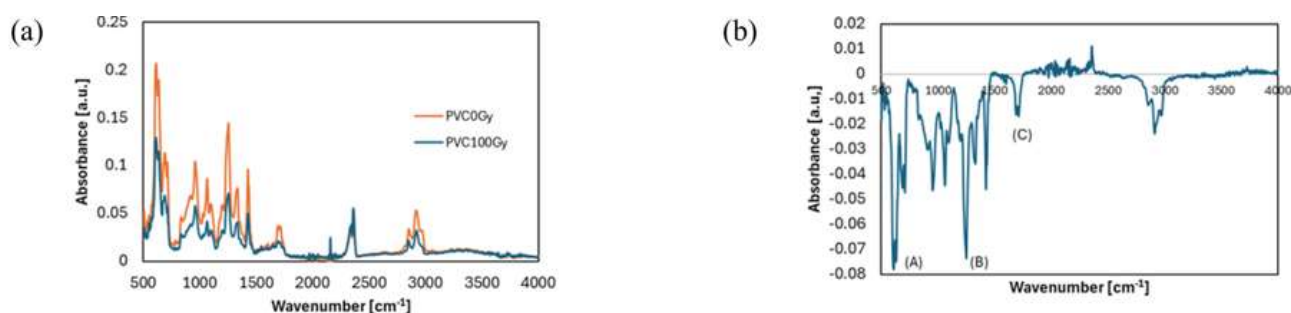


Fig. 7. (a) FTIR spectra of PVC containing 1 wt% benzoic acid before and after 100-Gy irradiation and (b) difference FTIR spectrum. (A) C–Cl stretching vibration, (B) C–O stretching vibration, (C) C=O stretching vibration.

4. Conclusions

Organic RPL materials were designed by focusing on reactions of radicals generated by X-ray irradiation and benzoic acid to form fluorescent molecules such as salicylic acid. Benzoic acid was dispersed in PVA, PMMA, or PVC. The RPL characteristics were evaluated by measuring the photoluminescence spectra before and after X-ray irradiation. In both the PVA samples before and after X-ray irradiation, the emission peak was observed at 412 nm and is attributed to salicylic acid. The photoluminescence intensity increased with increasing irradiation dose due to the formation of salicylic acid. At the optimal benzoic acid concentration of 1 wt%, the linear response range was 0–60 Gy. In both the PMMA samples before and after X-ray irradiation, the emission peak at 435 nm was observed and is attributed to benzoic acid tetramers. The photoluminescence intensity increased with increasing irradiation dose. This increase in intensity is possibly attributed to the restriction of

molecular motion caused by the oxidation of PMMA and suppression of non-radiative relaxation, thereby improving the photoluminescence efficiency of the benzoic acid tetramers. At the optimal benzoic acid composition of 1 wt%, the linear range was 0–100 Gy. In both PVC samples before and after X-ray irradiation, the emission peak was observed at 435 nm and is attributed to benzoic acid tetramers. The photoluminescence intensity decreased with increasing irradiation dose due to the decomposition of benzoic acid tetramers. The radiation-induced reactions in the PMMA and PVA samples can potentially be utilized as the operating principle for organic RPL dosimeters.

Acknowledgements

This research was supported by a Grant-in-Aid for Scientific Research (A) (No. 22H00308: 2022–2025). Part of this study was supported by the Cooperative Research Project of the Research Center for Biomedical Engineering of the Ministry of Education, Culture, Sports, Science, and Technology.

References

- [1] Rajamanickam Baskar, Kuo Ann Lee, Richard Yeo, Kheng-Wei Yeoh, *Int. J. Med. Sci.* 9 (2012) 193-199. DOI: [10.7150/ijms.3635](https://doi.org/10.7150/ijms.3635).
- [2] Krishna Koka, Amit Verma, Bilikere S. Dwarakanath, Rao V. L, Papineni, *Cancer Manag. Res.* 14 (2022) 1421-1429. DOI: [10.2147/CMAR.S351744](https://doi.org/10.2147/CMAR.S351744).
- [3] Cyrus Chargari, Eric Deutsch, Pierre Blanchard, Sebastien Gouy, *CA. Cancer J. Clin.*, 69 (2019) 386-401. DOI: [0.3322/caac.21578](https://doi.org/0.3322/caac.21578).
- [4] W. J. G. Oyen, L. Bodei, F. Giammarile, H. R. Maecke, J. Tennvall, M. Luster, B. Brans, *Ann. Oncol.* 18 (2007) 1782-1792. DOI: [10.1093/annonc/mdm111](https://doi.org/10.1093/annonc/mdm111).
- [5] Byungchul Cho, *Radiat. Oncol. J.*, 36 (2018) 1-10. DOI: [10.3857/roj.2018.00122](https://doi.org/10.3857/roj.2018.00122).
- [6] Laura A. Dawson, Michael B. Sharpe, *Lancet Oncol.*, 7 (2006) 848-858. DOI: [10.1016/S1470-2045\(06\)70904-4](https://doi.org/10.1016/S1470-2045(06)70904-4).

- [7] Daniel A. Low, Jean M. Moran, James F. Dempsey, Lei Dong, Mark Oldham, *Med. Phys.* , 38 (2011) 1313-1338. DOI: [10.1118/1.3514120](https://doi.org/10.1118/1.3514120).
- [8] E. M. Benítez, F. J. Casado, S. García-Pareja, J. A. Martín-Viera, C. Moreno, V. Parra, *Radiat. Meas.*, 58 (2013) 79-86. DOI: [10.1016/j.radmeas.2013.08.009](https://doi.org/10.1016/j.radmeas.2013.08.009).
- [9] Nikolina Vicoroski, Anthony Espinoza, Mitchell Duncan, Bradley M. Oborn, Martin Carolan, Peter Metcalfe, David Menichelli, Vladimir L. Perevertaylo, Michael L. F. Lerch, Anatoly B. Rosenfeld, Marco Petasecca, *Med. Phys.*, 44 (2017) 5402-5412. DOI: [10.1002/mp.12469](https://doi.org/10.1002/mp.12469).
- [10] David Lewis, Andre Micke, Xiang Yu, Maria F. Chan, *Med. Phys* 39 (2012) 6339-6350. DOI: [10.1118/1.4754797](https://doi.org/10.1118/1.4754797).
- [11] Xiangyu Ou, Xue Chen, Xianning Xu, Lili Xie, Xiaofeng Chen, Zhongzhu Hong, Hua Bai, Xiaowang Liu, Qiushui Chen, Huanghao Yang, *Research*, 2021 (2021) 9892152. DOI: [10.34133/2021/9892152](https://doi.org/10.34133/2021/9892152).
- [12] Yüksel Özdemir, Murat Kurudirek, *Ann. Nucl. Energy*, 36 (2009) 1769-1773. DOI: [10.1016/j.anucene.2009.09.008](https://doi.org/10.1016/j.anucene.2009.09.008).
- [13] Yuta Hiramatsu, Genichiro Wakabayashi, Masanori Koshimizu, *J. Mater. Sci. Electron.*, 37 (2026) 476. DOI: [10.1007/s10854-026-17233-9](https://doi.org/10.1007/s10854-026-17233-9).
- [14] Lifang Yuan, Yahong Jin, Yue Su, Haoyi Wu, Yihua Hu, Shihe Yang, *Laser Photonics Rev.* 14 (2020) 2000123. DOI: [10.1002/lpor.202000123](https://doi.org/10.1002/lpor.202000123).
- [15] T. Yamamoto, D. Maki, F. Sato, Y. Miyamoto, H. Nanto, T. Iida, *Radiat. Meas.* 46 (2011) 1554-1559. DOI: [10.1016/j.radmeas.2011.04.038](https://doi.org/10.1016/j.radmeas.2011.04.038).
- [16] C. Furetta, M. Prokic, R. Salamon, V. Prokic, G. Kitis, *Nucl. Instrum. Methods Phys. Res. A*, 456 (2001) 411-417. DOI: [10.1016/S0168-9002\(00\)00585-4](https://doi.org/10.1016/S0168-9002(00)00585-4).
- [17] V. Altunal, V. Guckan, A. Ozdemir, Y. Zydachevskyy, Y. Lawrence, Y. Yu, Z. Yegingil, *J. Lumin.* 241 (2022) 118528. DOI: [10.1016/j.jlumin.2021.118528](https://doi.org/10.1016/j.jlumin.2021.118528).
- [18] Peta Lonski, Tomas Kron *Front. Oncol.*, 12 (2022) 918178. DOI: [10.3389/fonc.2022.918178](https://doi.org/10.3389/fonc.2022.918178).

- [19] Takayoshi Yamamoto, Yuka Yanagida-Miyamoto, Toshiyuki Iida, Hidehito Nanto, *Radiat. Meas.*, 136 (2020) 106363. DOI: 10.1016/j.radmeas.2020.106363.
- [20] Dong Wook Kim, Jiwon Sung, Jaeman Son, Han-Back Shin, Min-Joo Kim, Yu-Yun Noh, Hojae Kim, Min Cheol Han, Jihun Kim, Su Chul Han, Kyung Hwan Chang, Hojin, Kim, Kwangwoo Park, Dongho Shin, *PLoS ONE* 15 (2020) e0234829. DOI: 10.1371/journal.pone.0234829.
- [21] W. A. Armstrong, D. W. Gran, *Nature* 182 (1958) 747. DOI: 10.1038/182747a0.
- [22] W. A. Armstrong, R. A. Facey, D. W. Grant, W. G. Humphreys, *Can. J. Chem.*, 41 (1963) 1575. DOI: 10.1139/v63-215.
- [23] R. W. Matthews, *Int. J. Appl. Radiat. Isot.*, 31 (1980) 585. DOI: 10.1016/0020-708x(80)90105-2.
- [24] A. K. Collins, G. M. Makrigiorgos, G. K. Svensson, *Med. Phys.*, 21 (1994) 1741. DOI: 10.1118/1.597275.
- [25] Peter A. Sandwall, Henry B. Spitz, Howard R. Elson, Michael A. S. Lamba, William B. Connick, Henry Fenichel, *J. Radioanal. Nucl. Chem.*, 307 (2016) 2505. DOI: 10.1007/s10967-015-4563-x.
- [26] Takuya Maeyama, Shinnosuke Hase, *Radiat. Phys. Chem.*, 151 (2018) 42. DOI: 10.1016/j.radphyschem.2018.05.009.
- [27] Zahra Alyani Nezhad, Ghazale Geraily, *Appl. Radiat. Isot.*, 179 (2022) 110015. DOI: 10.1016/j.apradiso.2021.110015.
- [28] Molham M. Eyadeh, Khalid A. Rabach, Dua'a I. Bani Hamdan, Ali M. Almomani, *Radiat. Meas.*, 192 (2026) 107622. DOI: 10.1016/j.radmeas.2026.107622.
- [29] Ritsuha Tanaka, Masanori Koshimizu, Ichiro Kawamura, Yutaka Fujimoto, Keisuke Asai, *J. Mater. Sci. Electron.*, 33 (2022) 3938. DOI: 10.1007/s10854-021-07588-6.
- [30] Ritsuha Tanaka, Masanori Koshimizu, Yutaka Fujimoto, Keisuke Asai, *J. Lumin.*, 264 (2023) 120166. DOI: 10.1016/j.jlumin.2023.120166.
- [31] Ritsuha Tanaka, Masanori Koshimizu, Akito Watanabe, Yutaka Fujimoto, Hiroki Kawamoto, Keisuke Asai, *J. Lumin.*, 267 (2024) 120367. DOI: 10.1016/j.jlumin.2023.120367.
- [32] Masanori Koshimizu, *Radiat. Meas.*, 176 (2024) 107222. DOI: 10.1016/j.radmeas.2024.107222.

- [33] Jay A. LaVerne, Eduardo A. Carrasco-Flores, M. S. Araos, Simon M. Pimblott, *J. Phys. Chem. A*, 112 (2008) 3345–3351. DOI: 10.1021/jp7113972.
- [34] Ichiro Sakurada, Syuzi Matsuzawa, *Kobunshi Kagaku* (in Japanese), 17 (1960) 268-272. DOI: 10.1295/koron1944.17.268.
- [35] W. A. Armstrong,, D. W. Grant, *Can. J. Nature*. 182 (1958) 747. DOI: 10.1139/v60-121.
- [36] Patrícia S. M. Santos, Helena B. Cardoso, Teresa A. P. Rocha-Santos, Armando C. Duarte, *Environ. Pollut.*, 244 (2019) 693-704. DOI: 10.1016/j.envpol.2018.10.059.
- [37] Hiroaki Baba, Michio Kitamura, *J. Mol. Spectrosc.*, 41 (1972) 302-309. DOI: 10.1016/0022-2852(72)90208-1.
- [38] Weiwei Tang, Mingtao Zhang, Huaping Mo, Junbo Gong, Jingkang Wang, Tonglei Li, *Cryst. Growth Des.* 17 (2017) 5049-5053. DOI: 10.1021/acs.cgd.7b01078.
- [39] Jiri Sturala, Marc K. Etherington, Aisha N. Bismillah, Heather F. Higginbotham, William Trewby, Juan A. Aguilar, Elizabeth H. C. Bromley, Alyssa-Jennifer Avestro, Andrew P. Monkman, Paul R. McGonigal, *J. Am. Chem. Soc.* 139 (2017) 17882–17889. DOI: 10.1021/jacs.7b08570.
- [40] Tomoaki Hinoue, Yuta Shigenoi, Misa Sugino, Yuji Mizobe, Ichiro Hisaki, Mikiji Miyata, Norimitsu Tohnai, *Chem. Eur. J.* 18 (2012) 4634-4643. DOI: 10.1002/chem.201103518.
- [41] N. V. Bhat, M. M. Nate, M. B. Kurup, V. A. Bambole, S. Sabharwal, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 237 (2005) 585-592. DOI: /10.1016/j.nimb.2005.04.058.
- [42] Toru Yahagi; Asuka Fujii, Takayuki Ebata, Naohiko Mikami, *J. Phys. Chem. A*, 105 (2001) 10673–10680. DOI: 10.1021/jp0126199.
- [43] Shiv Govind Prasad, Chhagan Lal, *Biointerface Res. Appl. Chem.* 13 (2022) 184. DOI: 10.33263/BRIAC132.187.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [supportinginfomation.docx](#)