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Photochromic Zirconium-Based Coordination Polymer for Colorimetric Dosimetry of Absorbed Gamma Radiation Dose.

Karim gado[1*], Ramy Abdlaty[1], Osama AbuZalat[1], Hesham Ramzy Tantawy[1] and A. A. Baraka[1]

[1] Military Technical College, Cairo, Egypt.
*Corresponding author: **Karimgado57@gmail.com**

Abstract. This research reports preparation and characterization of a coordination polymer and its use in a radiation dosimeter. Polymer preparation and characterization included X-ray diffraction (XRD), FTIR, SEM, and X-ray photoelectron spectroscopy (XPS). Dosimetry performance was examined through irradiation of the polymer with gamma radiation and observation of its optical performance with a hyperspectral camera. Observations showed a definite quenching behaviour under stimulation with UV, and a considerable hue variation under irradiation with gamma radiation. Observations confirm the viability of synthesized coordination polymer as a reliable radiation dosimeter, offering a new radiation tracking and detection mechanism.

1. Introduction

Radiation detection techniques have seen massive growth in the last decades. However, there are many distinct types of detectors, such as ionizing chambers and scintillators (the most prevalent in radiation detection instruments)[1], which are designed to produce a strong light output with a quick response time, providing data that allows the quantification of radiation sources. Currently, semiconductor detectors offer the highest resolution sensors. Most of these detectors have many problems, as they are expensive, have low sensitivity to noncharged radiation like Gamma rays, and have extended response times [2]. Therefore, it is very desirable and urgent to require a rapid and sensitive method for the detection of radiation, especially γ-ray radiation [3].

Another type of radiation detector is radiochromic films, which make a visible change in film color when subjected to radioactive materials. Still, this technique has many disadvantages, such as it is a qualitative analysis, not a quantitative one [4].

One of the recent techniques that are used in radiation detection is Radio-Photoluminescence materials; a new type of these materials is MOFs, which have interesting properties such as scintillation and semi-conductivity that can be used in radiation detection[5].

Metal-organic frameworks (MOFs) or coordination polymers (CPs) are synthesized from the coordination bonding between metal ions, usually a transition metal, and a variety of organic linkers; this variety of linkers and metal ions gives them the tunability in their structure, which is reflected in their outstanding properties, such as high porosity, high surface area, crystallinity, semi conductivity, and fluorescence[6].

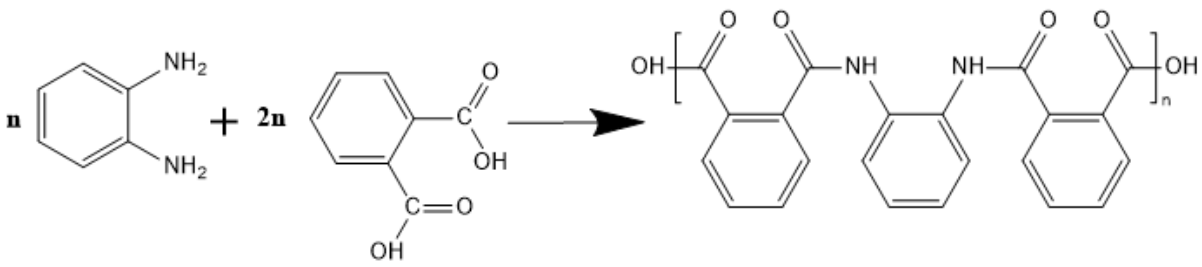
They have many applications, such as catalysts, medicine carriers, adsorbents, gas storage, sensing, and radiation detection. Their strong network structure makes them very stable under very high doses of radiation, exceeds their limitation, and the conjugation in the organic linker gives them strong luminescence under excitation with light.
When subjected to radiation, Radio Photoluminescent MOFs cause excitation and de-excitation processes, which change luminescence intensity, that a colorimetric change in the visible or UV range may accompany. This makes them promising dosimetry platforms for radiation detection. A relation between normalized emission luminescence intensity after being radiated and the respective radiation dose can be used to establish a relationship that can be used as a quantitative chemical dosimeter for γ-radiations [7].

This work reports the synthesis and structural characterization based on Zr(IV) as a metal ion node and a synthesized organic linker reported before in our previous work. [8]. The obtained coordination polymer was found to have fluorescence under excitation with UV light with a wavelength of 365 nm. Studying the effect of radiation on it was done under different radiation doses.
It was found that its fluorescent intensity changes with the amount of accumulated dose. A linear relation between the dose absorbed and the emission fluorescent intensity was set up, which gives a colorimetric change response in a chromaticity diagram (CIE). This change was visible under UV light.

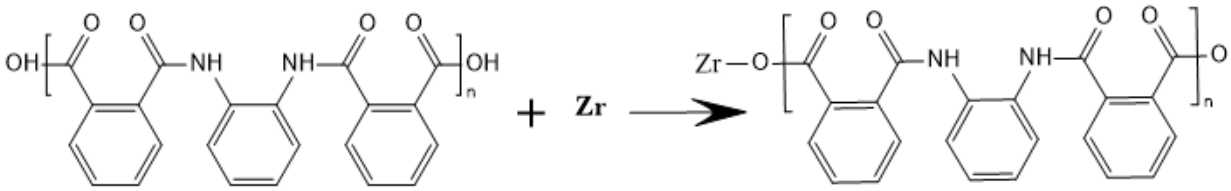
2. Materials and method

2.1. Materials and synthesis procedure

All materials are from commercial suppliers without any purification processes: O-phenylene diamine (99%), phthalic acid (99%), zirconium oxychloride (98%), and DI-water. First, the organic linker is to be prepared by the amidation reaction according to scheme 1. Typically, Phthalic acid (0.2 mmol) and O-phenylene diamine (0.1 mmol) were dissolved separately in DI water (20 ml) and heated at 70°C for 20 minutes. Then, the two solutions were mixed, and the mixture was also heated for about 30 minutes to produce the water-soluble linker (OC-AMAM-CO).
For solvothermal synthesis, the CP, zirconium oxychloride (0.1 mmol, in 20 ml DI water) was added to (OC-AMAM-CO) linker solution and the whole mixture was left at the same temperature (70°C) for 8 hours where the Zr-(OC-AMAM-CO) product in the form of fine powder was precipitated, Scheme 2. The powder precipitation was separated from the liquor solution by decantation and filtration and then washed with DI-water 5 times to get rid of any reactants residuals and left to dry in an oven at 70°C for 24 hours.



Scheme 1. Amidation reaction of O-phenylene diamine and phthalic acid to produce (OC-AMAM-CO)



Scheme 2. Proposed coordination of Zr (IV) with linker (OC-AMAM-CO) producing Zr-(OC-AMAM-CO)

2.2. Characterization of (OC-AMAM-CO) linker and Zr-(OC-AMAM-CO)

To chemically characterize the (OC-AMAM-CO) linker and the Zr-(OC-AMAM-CO) CP, FTIR standard KBr disk method using Jasco FT/IR 4100 in the 4000−400 cm−1 range. Scanning electron microscope SEM (Zeiss EVO-10 microscopy) is used to determine and analyze the morphologies of the Zr coordination polymer. X-ray diffraction (XRD, Shimadzu XD-l) was also used to study the crystallinity, A hyperspectral camera collects absorption spectra after irradiation with γ-rays and fluorescence spectra under ultraviolet light (365 nm).

2.3. Gamma dosimetry experiment

Six samples of the same synthesis conditions and amount were subjected to γ-rays irradiation in a gamma chamber at different exposure times to obtain different absorbed doses. Furthermore, the samples were measured under a hyperspectral camera, visible and UV light. The following setup was used to get the luminescence spectra of irradiated samples with different doses as shown in Figure 1. The luminescence spectra were measured, one without excitation by UV (365 nm) and the other with it.

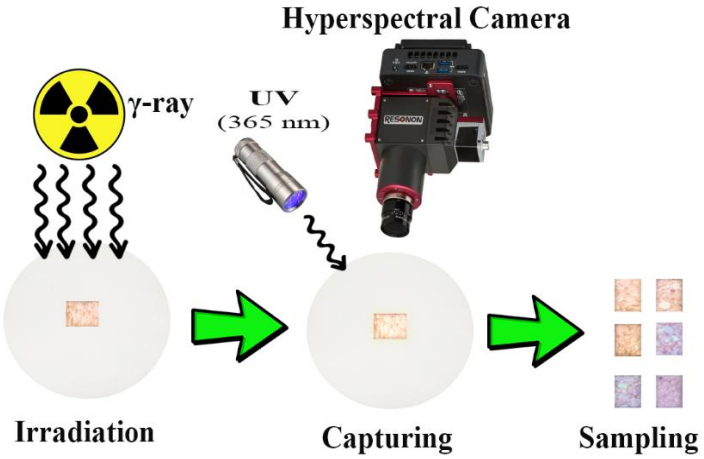


Figure 1. The setup used to obtain emission spectra.

3. Results and discussions

3.1. Characterization of Zr-(OC-AMAM-CO) CP

Figure 2 shows the FTIR spectra for (Phthalic acid (Ph), O-phenylene diamine (O-ph), (OC-AMAM-CO) linker, and synthesized Zr-(OC-AMAM-CO) CP. The FTIR results for the precursors (Ph, O-Ph) and the (OC-AMAM-CO) linker aligned with those previously reported [8] . for the FTIR spectrum of the Zr-(OC-AMAM-CO) CP, the peak at 450 cm^{-1} corresponds to the Zr-

O bond [9] also the presence of some peaks from the (OC-AMAM-CO) linker suggests the successful formation of the CP from the suggested linker.

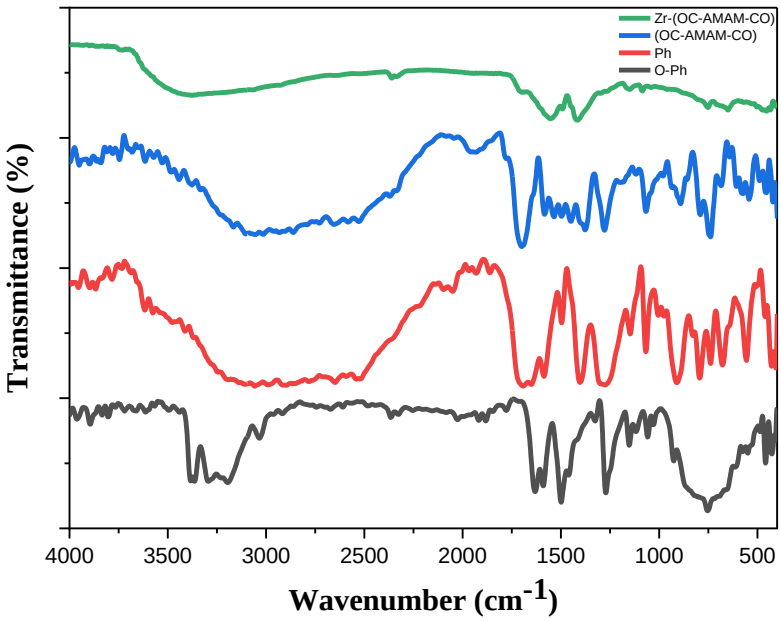


Figure 2. FTIR spectra for (Phthalic acid (Ph), O-phenylene diamine (O-ph), (OC-AMAM-CO) linker, and synthesized Zr-(OC-AMAM-CO) CP

An X-ray diffraction (XRD) examination was performed to examine the crystallinity and phase composition of the precursor materials, the synthesised (OC-AMAM-CO) linker, and the resultant Zr-(OC-AMAM-CO) CP. The diffraction patterns of phthalic acid and o-phenylenediamine display distinct peaks, signifying their crystalline characteristics. The creation of the (OC-AMAM-CO) linker results in a significant broadening of peaks, indicating a reduction in crystalline, perhaps due to molecular interactions and structural alterations caused by the reaction. The XRD pattern of the final Zr-(OC-AMAM-CO) CP exhibits notable peak shifts and novel diffraction characteristics relative to the precursors, hence validating the successful emergence of a new crystalline phase. The absence of specific precursor peaks and the advent of new reflections further corroborate the structural shift. The extensive background signal in the polymer pattern indicates partial

amorphization or diminished long-range order, a phenomenon frequently observed in coordination polymers [10, 11].

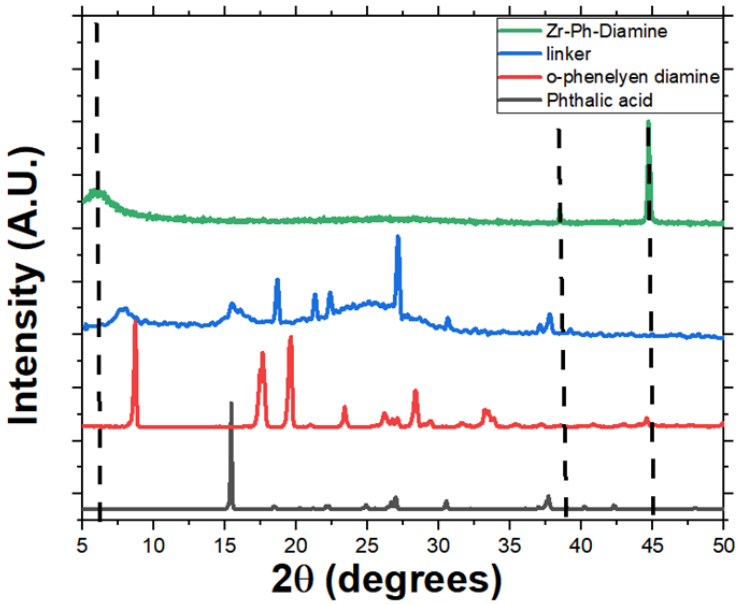


Figure 3. XRD spectrum of Ph, O-ph (OC-AMAM-CO), and Zr-(OC-AMAM-CO) CP

A comprehensive SEM analysis was conducted in an attempt to study the microstructure of synthesized Zr-(OC-AMAM-CO) CP in detail. As can be seen in Figure 4, SEM micrograph reveals a complex microstructure with particles having an irregular shape and a wide distribution in terms of size, ranging from sub-micrometer to several micrometers in dimensions. Particles' surfaces exhibit roughness, indicative of a high specific surface area. The presence of observed particles' agglomeration could arise from the intrinsic property of the coordination polymer, but could also arise during preparation techniques adopted in the fabrication of the under investigation samples, too [12].

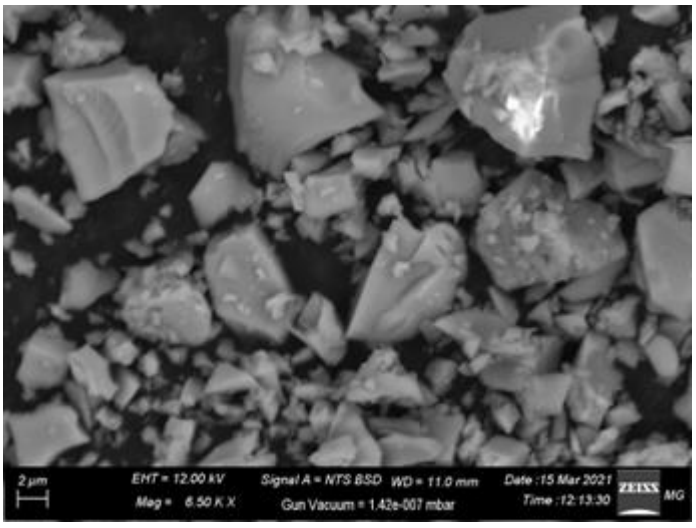


Figure 4. SEM images of Zr-(OC-AMAM-CO) CP

3.2. Effect of gamma radiation on Zr-(OC-AMAM-CO) and dosimetry

The effect of gamma radiation on the chemistry of Zr-(OC-AMAM-CO) was investigated by recording FTIR spectra of the samples irradiated by different doses: 1, 5, 30, 50, and 80 kGy.

Fig. 5 shows the FTIR spectrum of the radiated samples along with the spectrum of the non-irradiated sample, where some apparent changes can be observed upon irradiation. The figure shows a general fading of peaks' strengths for all functional groups as the absorbed dose increases. This fading should indicate some disintegration of these groups by the action of gamma rays. Also, in general, interestingly, there are blue shifts for almost all significant peaks. This weakening of peaks indicates potential breaking of bonds or structural changes within the polymer due to radiation exposure[13]. Additionally, the observation of blue shifts for almost all significant peaks is noteworthy. Blue shifts in the FTIR spectrum typically indicate changes in the vibrational frequencies of the functional groups, which can be attributed to alterations in the electronic environment or bonding characteristics caused by the radiation. These shifts and changes in peak intensities provide insight into the possible structure deterioration after gamma radiation exposure [14].

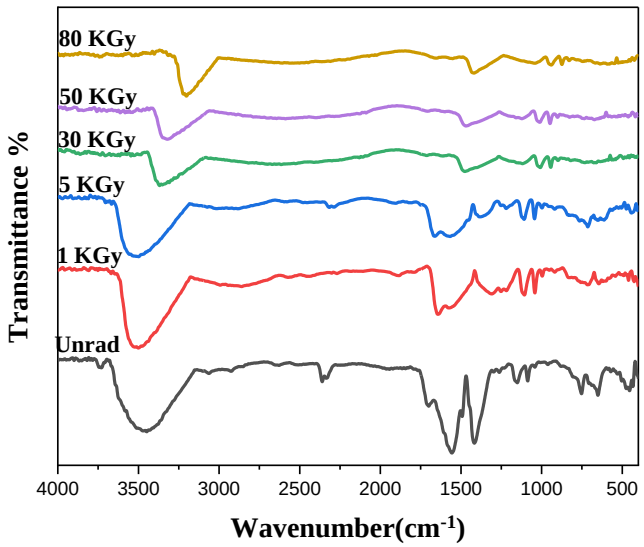


Figure 5. FT-IR spectra for MOF at different irradiation doses

3.3. Spectroscopic Properties of Zr-(OC-AMAM-CO) CP

The hyperspectral analysis performed in the Zr-(OC-AMAM-CO) CP reveals a uniform absorption at 470 nm in irradiated and unirradiated samples, and in so doing, confirms an intrinsic optical stability feature of the CP as shown in fig.6. This absorption can most probably be credited to electronic excitations about the organic linker or coordination environment of zirconium metal sites. Also, the absorbance intensity decreased with increasing radiation dose. This indicates that the material has become darker because of radiation but still has the same characteristic absorption peak. The darkening effect could be attributed to structural or electronic changes within the Zr-(OC-AMAM-CO) CP caused by radiation exposure, which impacts its optical properties. Despite these changes, the retention of the characteristic absorption peak indicates that the fundamental structure of the polymer remains intact.

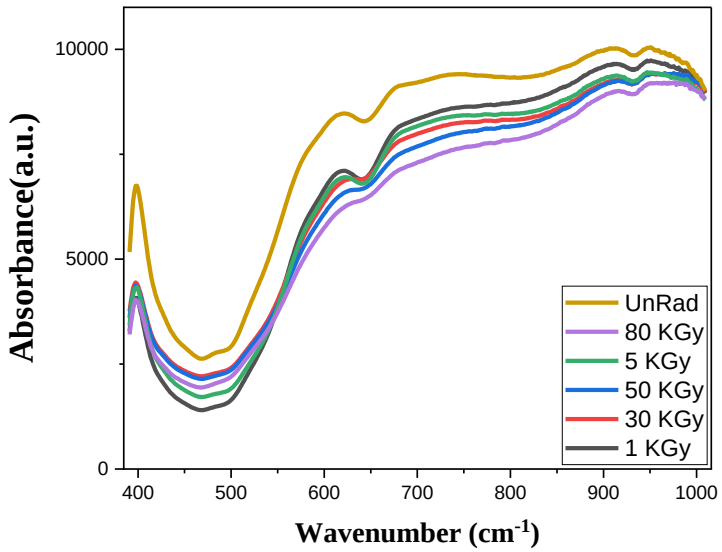


Figure 6. Absorption of Zr-(OC-AMAM-CO) CP

Figure (7) shows that the emission spectra of the Zr-(OC-AMAM-CO) CP shifts from 560 nm to 587 nm as shown in CIE in the figure below with increasing radiation doses, indicating a change in the electronic environment of the material, likely due to the interaction with gamma radiation. This redshift in the emission peak can suggest structural or compositional changes within the coordination polymer, which was confirmed by the results of the FTIR spectrum of the radiated samples.

The gradual decrease in fluorescence intensity with increasing radiation dose, while maintaining a linear relationship, suggests that the luminescence quenching is dose-dependent and can be used to quantitatively measure the absorbed radiation dose. This behavior is characteristic of a good dosimeter, as it provides a clear and quantifiable response to varying levels of radiation exposure.

The more interesting part is that the samples had a color change, which was also proportional to the amount of absorbed dose. So, there is a dual change in luminescence and color.
This dual change in both luminescence and color of the Zr-(OC-AMAM-CO) CP upon exposure to gamma radiation is a particularly intriguing aspect of this study. This dual response mechanism enhances the potential applicability of the CP as a radiation dosimeter. The color change offers a straightforward visual cue that can be easily observed without specialized equipment, while the luminescence change provides a more precise quantitative measure of the absorbed dose. This combination of qualitative and quantitative detection makes the Zr-(OC-AMAM-CO) CP a versatile tool for various radiation monitoring applications. Such features could prove invaluable in environments where rapid and accurate radiation assessment is critical [15].

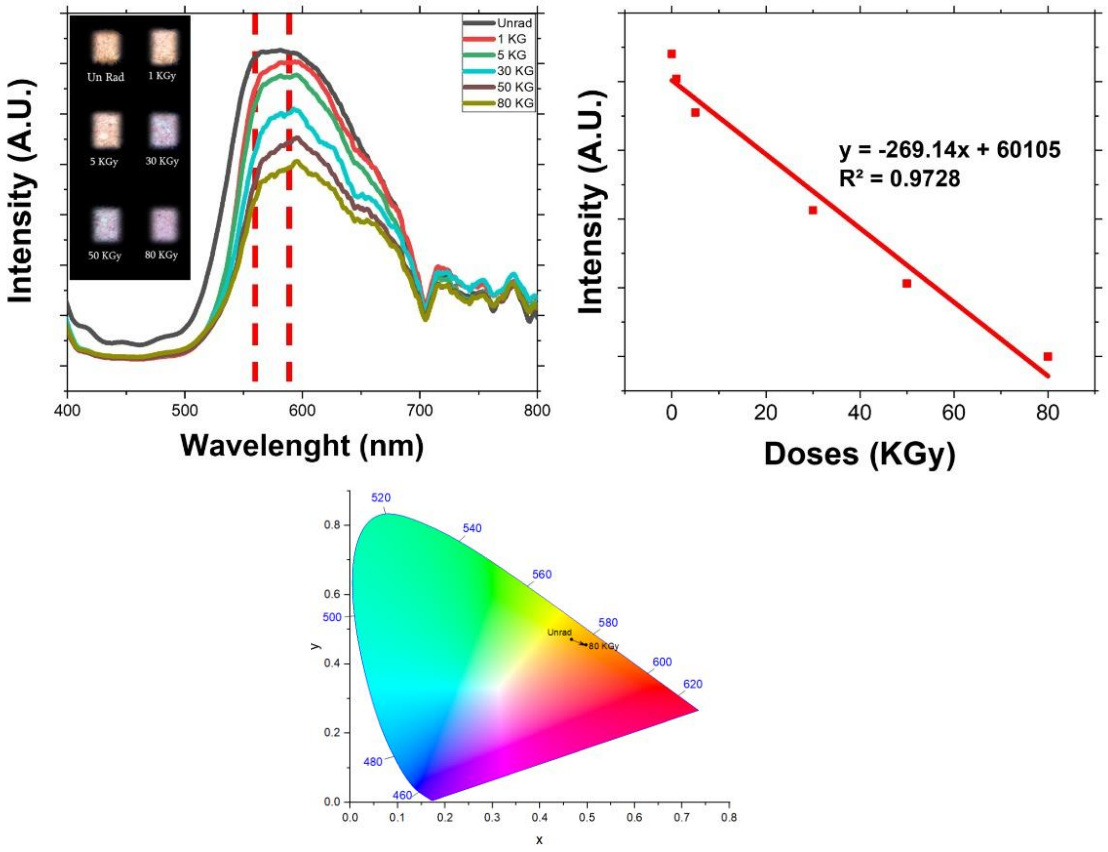


Figure 7. (A) Dose dependence of emission spectra for irradiated samples under UV (365 nm). (B) CIE coordinates are calculated using the software GoCIE corresponding to emission spectra.

4. Conclusion

In conclusion, the synthesized coordination polymer exhibits promising dosimetric properties, making it a potential candidate for radiation detection applications. The observed quenching effect and color shift upon gamma exposure provide a straightforward and effective means of radiation monitoring. The combination of advanced characterization techniques confirms the material's structural integrity and responsiveness to radiation. Additionally, the Zr-(OC-AMAM-CO) CP's ability to undergo a distinct optical transition upon radiation exposure suggests potential applications in real-time radiation sensing and monitoring. The linear relationship between the absorbed radiation dose and emission fluorescence intensity further supports its quantitative detection capability. Future research could explore the Zr-(OC-AMAM-CO) CP's performance under different types of radiation and its integration into portable detection devices, enhancing its practicality and accessibility in various radiation monitoring scenarios. General, the study demonstrates the potential of Zr-(OC-AMAM-CO) as an innovative tool for ensuring safety and accuracy in radiation environments.

5. References

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