DEVELOPMENT OF NOVEL GAMMA RADIATION DOSIMETER BASED ON METALLOPHTHALOCYANINE

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Abstract
In this study, zinc phthalocyanine was evaluated as a possible chemical dosimeter for gamma rays at low-medium dose ranges in solution form and PVA film. The zinc phthalocyanine was successfully synthesized with a high yield under microwave irradiation at 200 °C. The calibration curves of absorbance versus dose of gamma irradiation show excellent linearity over a wider dose range (1 - 25kGy). After being irradiated, the samples' color changed from blue to yellow.

Introduction
Dosimetry is an essential element in the quality control of radiation processing, assuring the correct and uniform supply of radiation doses to a given area. As a result, a variety of dosimetry systems with various dosage sensitivities and dose ranges are utilized for common radiation applications[1]. Such systems present different types of radiochromic solution, gel, and film dosimeters that can be used in low-dose radiotherapy dosimetry due to direct radiation-induced permanent change in the color of dyed materials[2], and high-dose radiation applications such as sterilization, food irradiation, polymers applications, and agriculture[3]. Importantly, the degree of coloration is proportional directly to the amount of absorbed dose[4].
Organic dyes are among the most studied and used chemical dosimeters[5,6]. They have been utilized in solution form or embedded in various polymeric films to measure the distribution of the absorbed dose. These radiochromic thin film dosimeters are often used in radiation processing for routine dose control during gamma and electron-irradiation. The least researched dosimeters among the organic dyes are metallophthalocyanines (MPcs)[7,8], a symmetrical 18π-electron aromatic macrocycle. Their attractive color, together with tremendous chemical and thermal stability, has led us to research more reliable, stable, and less expensive dosimeter systems.
The present work aims to investigate the response of the change in the absorbance versus gamma-irradiation at low-medium dose ranges for zinc phthalocyanine (ZnPc). Microwave-assisted synthesis of ZnPc was successfully performed in a mono-mode microwave reactor at 200 °C. Organic dye has been utilized in the solution or embedded in a polymeric film for dosimetry application.

Experimental
All chemicals: zinc (II) acetate dihydrate, $Zn(CH_3CO_2)_2 \cdot 2H_2O$ (>99%, Sigma-Aldrich), 1,2-dicyanobenzene, $C_6H_4(CN)_2$ (≥98%, Sigma-Aldrich), 2,2,6,6-tetramethylpiperidine, TMP (≥99%, Sigma-Aldrich), polyvinyl alcohol, PVA (95.5-96.5% hydrolyzed, M.W. approx. 85 000-124 000, Sigma-Aldrich), *N*, *N*-dimethylformamide, DMF (>99%, Alfa Aesar), dimethyl sulfoxide, DMSO (>99%, Fisher Chemicals), and methanol (≥ 99%, Sigma Aldrich) were of

the highest purity commercially available and were used without further purification. Mili-Q deionized water (electrical resistivity = 18.2 MΩ cm^{-1}) was used.

Microwave-assisted synthesis of ZnPc ($ZnPc_{MW}$): The starting compounds 1,2-dicyanobenzene (2.5 mmol, 0.327 g) and zinc (II) acetate dihydrate (0.625 mmol, 0.137 g) were dissolved in 1 mL of DMF. The catalyst TMP was added to the reaction mixture under stirring (100 μL). The microwave reaction mixture was irradiated at T = 200 °C ($ZnPc_{MW}$) for 5 min and after cooling to room temperature, the precipitate was filtered off and washed with 3% HCl, water, and methanol, and dried in an oven at T = 60 °C. The resulting deep purple crystals remain after the processing of the reaction mixtures. Yield (68%).
ZnPc/PVA films were prepared by dispersing 4 mL of ZnPc ($1x10^{-4}$M, DMSO) in the 6 mL of 6% PVA/DMSO solution by sonication for 30 min to get a perfectly homogeneous solution. Afterwards, 10 mL of each mixture was poured into Petri dishes for film formation. Good quality and colored films of uniform surface finish were obtained within 8h of drying in a vacuum oven.

Microwave-assisted synthesis was performed in a mono-mode microwave reactor Anton Paar Monowave 300. X-ray diffraction (XRD) measurements were performed by SmartLab® X-ray diffractometer (Rigaku, Japan, www.rigaku.com) using Cu Kα radiation (λ = 1.542 Å). The patterns were collected at room temperature, within a 2θ range of 5–60° in a scan rate of 3°/min with divergent slit of 0.5 mm, operated at 40 kV and 30 mA. The surface morphology of the synthesized compounds was analyzed with atomic force microscopy (Quesant, Ambios Technology, USA) operating in tapping mode in air, at room temperature. Surface morphologies of the deposited samples were studied by Atomic Force Microscope (AFM), Quesant (Agoura Hills, CA, USA), which was operating in the tapping mode, in the air, at room temperature. Standard silicon tip (NanoAndMore Gmbh, Wetzlar, Germany) with the constant force of 40 N m^{-1} was used. Images were obtained at scan rate of 2Hz, with 512 x 512 pixels scan resolution over different square areas. The average size of objects in AFM images and average surface roughness were determined by Gwyddion software (https://www.degruyter.com/document/doi/10.2478/s11534-011-0096-2/html). Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopic measurements were performed in 400−4000 cm^{-1} range with a spectral resolution of 4 cm^{-1} at room temperature by Thermo Scientific Nicolet iS50 FT-IR spectrometer equipped with built-in all reflective ATR diamond. The ultraviolet-visible (UV/Vis) absorption spectra were recorded on Shimadzu 1800 UV–Vis spectrophotometer equipped with a temperature controller in the range of 200–800 nm. Prepared samples were irradiated by gamma ray flux ^{60}Co nuclide with a photon range of 1.3 MeV (Radiation unit located in Laboratory for radiation chemistry and physics "GAMA" in Vinča Institute of Nuclear Sciences, designed by the Commission Energie Atimique Conservatome from France).

Results and discussion

The phase identity and purity of synthesized $ZnPc_{MW}$ were investigated by XRD. As demonstrated in Figure 1., all of the $ZnPc_{MW}$ sample's reflection peaks could be indexed as β-ZnPc according to the JC-PDS card (No. 39-1882). No traces of any impurity phases were noticed indicating that the products were pure β-ZnPc crystals.

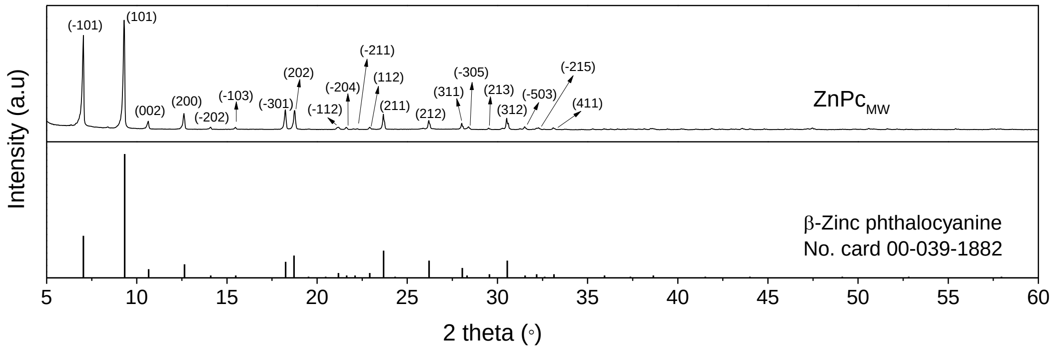

Figure 1. XRD pattern of $ZnPc_{MW}$.

The AFM surface morphologies (Figure 2.) show the flatness properties of the crystal face. The scanned surface in this AFM image is 8x8 µm^2, and in the inset we can see a zoomed surface of 2x2 µm^2. Average RMS surface roughness (calculated from several images covering 8x8 µm^2 surface area) is (124.6 ± 29) nm, the average length of crystals is (4.2 ± 0.8) µm, the average width is (2.4 ± 0.5) µm, and the average height is (0.43 ± 0.02) µm. The stacking structure of a planar $ZnPc_{MW}$ crystal strongly affects its high stability, due to π-π interaction between phthalocyanine moieties.

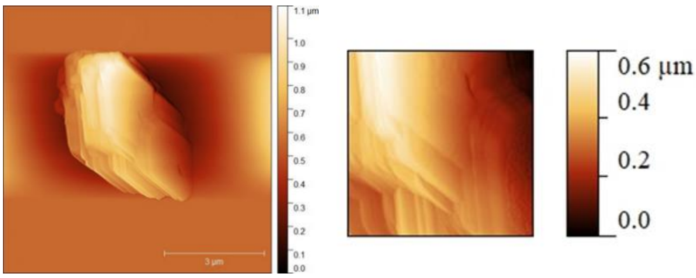

Figure 2. AFM image of $ZnPc_{MW}$ crystals.

The FT-IR spectral measurement is carried out to ascertain the functional group structures for ZnPc. The absence of the characteristic vibrations of C≡N and the appearance of the absorption peaks at 1480 cm^{-1}, 1452 cm^{-1}, 1330 cm^{-1}, 1162 cm^{-1}, 1115 cm^{-1}, and 886 cm^{-1} assigned to phthalocyanine skeletal vibration indicated that the final products were synthesized successfully. The peaks located at 1407 and 1283 cm^{-1} are assigned to the stretching vibration of the aromatic phenyl ring and C–N= covalent bond, respectively. The absence of metal-free Pcs characteristic absorption peak around 1000 cm^{-1} confirmed the reaction selectivity and purity of the synthesized compound.

Absorption spectra of gamma-irradiated zinc-based phthalocyanines in DMSO under dose at 1, 2, 3, 5, 7, 10, 15, and 25kGy are presented in the Figure 3a. and corresponding photos of the gamma-irradiated solutions are presented in the Figure 3b. There are two broad bands with maxima in the ultra-violet region at a wavelength of 342 nm and in the red region at a wavelength of 667 nm. Each spectrum corresponds to a typical shape for this class of compounds.

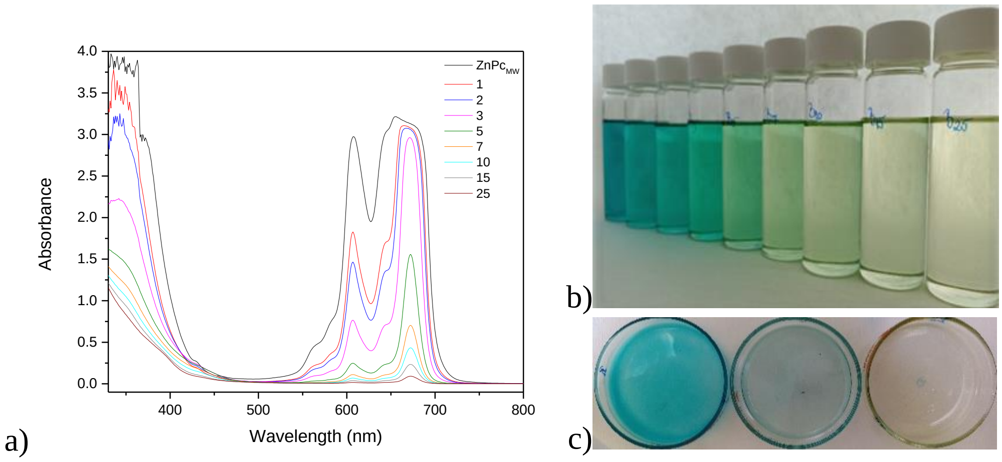

Figure 3. a) Absorption spectra of gamma-irradiated zinc phthalocyanine in DMSO under dose at 1, 2, 3, 5, 7, 10, 15, and 25kGy, and corresponding photos of b) gamma-irradiated zinc phthalocyanines solutions and c) selected ZnPc/PVA films.

The intense color of ZnPc is due mainly to the strong absorbance peak in the red region. Calibration curves of absorbance versus dose of gamma-irradiation demonstrate excellent linearity within the observed doses for all samples, confirming the applicability of the Beer-Lambert law and the absence of significant aggregation effects under gamma rays. The color of solutions is changed from blue to yellow under gamma-irradiation with different doses, which is a consequence of the intensity ratio and wide of the peaks from the second band, at wavelengths of 667 nm and 607 nm. The use of ZnPc/PVA films for dosimetry applications was successfully confirmed, as shown in Figure 3c. Selected solutions of ZnPc incorporated into PVA, irradiated at different doses of gamma irradiation, gave films with colored shades of blue, green, and yellow.

Conclusion

A new chemical dosimeter based on ZnPc has been introduced for gamma-irradiation applications. The compound was successfully synthesized under microwave irradiation. The solutions of organic dye were prepared in DMSO to study the effect of the degree of coloration on the dose response of the ZnPc solution dosimeter. Upon irradiation, the color of the samples changed from blue to yellow. The absorption spectra in the UV-Vis region reveal a gradual decrease of the absorption peak at wavelengths of 667 nm and 607 nm as the adsorbed dose increased up to 25kGy. The application of ZnPc/PVA films for radiation dose applications has been confirmed.

Acknowledgements

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References

[1] A.L. Melendez-Lopez, A. Paredes-Arriaga, J. Cruz-Castaneda, A. Negron-Mendoza, S. Ramos-Bernal, M. Colin-Garcia, A. Heredia, J. Nucl. Phys. Mat. Sci. rad. A. 6 (2018) 87.
[2] M.M. Eyadeh, K.A. Rabaeh, T.F. Hailat, F.M. Aldweri, Radiat. Meas. 108 (2018) 26.
[3] A. Raouafi, M. Daoudi, K. Jouini, K. Charradi, A.H. hamzaoui, P. Blaise, K. Farah, F. Hosni, Nucl. Instrum. Methods Phys. Res., Sect. B 425 (2018) 4.

[4] F.M. Aldweri, M.H. Abuzayed, M.S. Al-Ajaleen, K.A. Rabaeh, Results Phys. 8 (2018) 1001.
[5] M.A. Rauf, S. Salman Ashraf, J. Hazard. Mater. 166 (2009) 6.
[6] M.F. Barakat, K. El-Salamawy, M. El-Banna, M. Abdel-Hamid, A. Abdel-Rehim Taha, Rad. Phy. Chem. 61 (2001) 129.
[7] H.N. Raval, D.S. Sutar, V.R. Rao, Org. Elect. 14 (2013) 1281.
[8] N. Chaudhary, A. Singh, D.K. Aswal, A.K. Debnath, S. Samanta, S.P. Koiry, S. Sharma, K. Shah, S. Acharya, K.P. Muthe, S.C. Gadkari, Synth. Met. 231 (2017) 143.