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Poly [1,1'-bis(ethynyl)-4,4'-biphenyl(bis-tributylphosphine)Pt(II)] solutions used as low dose ionizing radiation dosimeter

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In this work, the effect of gamma radiation on the optical properties of polymetallayne poly[1,1'-bis(ethynyl)-4,4'-biphenyl(bis-tributylphosphine)Pt(II)] (Pt-DEBP) in chloroform solution is studied. The samples were irradiated at room temperature with doses from 0.01 Gy to 1 Gy using a ⁶⁰Co gamma ray source. A new band at 420 nm is observed in the emission spectra, in superposition to the emission maximum at 398 nm, linearly dependent on dose. We propose to use the ratio of the emission amplitude bands as the dosimetric parameter. This method proved to be robust, accurate, and can be used as a dosimeter in medical applications. © 2013 AIP Publishing LLC.
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Gamma radiation is widely employed in various ways, from medicine to food industry.^{1,2} Due to its potential danger to life, its use must be accompanied by strict control of the applied doses, as well as a control over the personnel who operates such equipments. In fact, the chemical and biological effects caused by ionizing radiation depend on the nature of the radiation employed and the exposed object/tissue. In particular, very accurate control of low doses is desired for medical applications, such as in the diagnosis and treatment of cancer or in personal dosimetry.

Most commonly, compounds based on inorganic crystals with high effective atomic number (Z_{eff}) are used as gamma ray detectors or dosimeters.^{1,3} However, the application of these materials has serious drawbacks, such as high cost, poor energy resolution, and restricted working conditions.³ For example, ZnCdTe can be operated at room temperature, but it is challenging to obtain large perfect crystals, which makes its use as dosimeter expensive. Scintillator of NaI (TI) detector works at room temperature, but its energy resolution is limited. Germanium crystals offer high energy resolution, but require low operating temperatures in liquid nitrogen.³

In this context, organic semiconductors (OS) have been considered interesting candidates to low dose radiation detection.⁴⁻⁶ In particular, it was reported that poly (2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) in halogenated aliphatic solvents, could be used as sensitive dosimeters. In this system (MEH-PPV/halogenated solvent), a blue shift in the main absorption peak is observed after exposure to ionizing radiation. This effect was attributed to a decrease in the polymer conjugation length, induced by radical incorporation (from the solvent radiolysis) in the polymer structure, enabling the detection of doses between 1 and 114 Gy.^{4,7,8} Since then, several studies have been published using OS in dosimetry.^{9,10} However, there is still no detection system using conjugated polymers that measures doses below 1 Gy.

We have recently proposed the use of organometallic polymer, i.e., $[-\text{Pt}(\text{PBu}_3)_2-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-]_n$ (Pt-DEBP) as dosimeters (structure shown in Fig. 2).^{11,12} Organometallic compounds like Pt-DEBP belong to a class of materials of great interest, mainly due to the transition metal in the main chain that gives unique optical and electrical properties.^{13,14} These compounds show a delocalized π -conjugated electronic system that extends from the polymer main chain to the d-orbitals of the metal. In particular, the use of these compounds in dosimetry is very promising, since their electronic transitions are mainly related to a mixture of metal-to-ligand charge transfer states (MLCT) and ligand centered charge transfer states (π - π^*), which confer high sensitivity of their opto-electronic properties to possible structural modifications.¹⁵⁻¹⁷

Changes in the absorption and emission spectra of Pt-DEBP chloroform solutions were observed after irradiation with doses up to 90 Gy. Similarly to MEH-PPV systems, the blue-shift in the absorption spectrum was attributed to chlorine incorporation on the polymer main chain.^{11,12} However, no systematic investigation was performed yet on the changes induced on the emission spectrum.

The evaluation of the emission spectrum is interesting because it is, in principle, more selective than absorption measurements. Indeed, the optical response can be adjusted by choosing the desired excitation, which allows filtering the most significant changes induced by the ionizing radiation.

In this report, we investigate the system Pt-DEBP/ CHCl_3 specifically for low dose dosimetry. Storage capabilities were also evaluated. Significant changes were observed and quantified in the emission spectrum of the system, which were stable even after 1 month. The results indicate that Pt-DEBP/ CHCl_3 can be used as a low dosimeter for medical applications and in personal dosimetry.

poly[1,1'-bis(ethynyl)-4,4'-biphenyl(bis-tributylphosphine)Pt(II)] with ten monomeric units (Pt-DEBP₁₀) was synthesized according to a procedure found in literature.¹³ Pt-

DEBP solutions in CHCl_3 (ACROS) were prepared at room temperature, under weak illumination conditions, to avoid polymer photodegradation. Solutions were kept in glass recipients (4 mL, Wheaton 13-425) and irradiated with a ^{60}Co gamma-ray source (1.25 MeV, SIEMENS GAMATRON S-80) with appropriate acrylic build-ups (thickness of 0.5 cm) in order to reach the necessary electronic balance as well to avoid backward irradiation. Pt-DEBP concentrations in solution varied from 0.0113 mg/mL to 0.0250 mg/mL. Samples were irradiated with doses ranging from 0.01 to 1.0 Gy at room temperature, in the dark, at a rate of 0.5 Gy/min. Measurements of UV-Vis spectroscopy have been performed on a Shimadzu UV mini 1240. Fluorescence measurements were made in a Varian Cary Eclipse fluorimeter, upon excitation at 390 nm. Samples were kept in the dark at 280 K (commercial refrigerator), in order to secure that the observed changes were solely due to exposure to ionizing radiations. No systematic study was performed, concerning the stability of Pt-DEBP at different temperatures, however, this polymer is known to be stable up to 423 K from TGA-DTA.¹³ We are assuming that the structural changes due to gamma irradiation are not changing this stability considerably.

Fig. 1 shows the absorption and emission spectra of Pt-DEBP in chloroform solution (0.0250 mg/mL) before and after irradiation with different doses from 0.1 to 0.8 Gy. The electronic absorption spectra of the polymer (see inset) show an intense absorption band at ca. 354-370 nm that is assigned to metal-to-alkynyl MLCT transitions.¹⁸ The principal absorption peak is due to $\pi \rightarrow \pi^*$ absorption localized on the conjugated system.¹⁸ The emission spectrum is composed of the singlet transitions between 400-450 nm and triplet emissions (phosphorescence) bands above 540 nm.^{11,18}

Note that no significant changes are observed in the absorption spectra in the dose range considered. On the other hand, major changes can be observed in the emission spectra with a clear increase in the intensity of the spectrum followed by the formation of a new band around 420 nm.

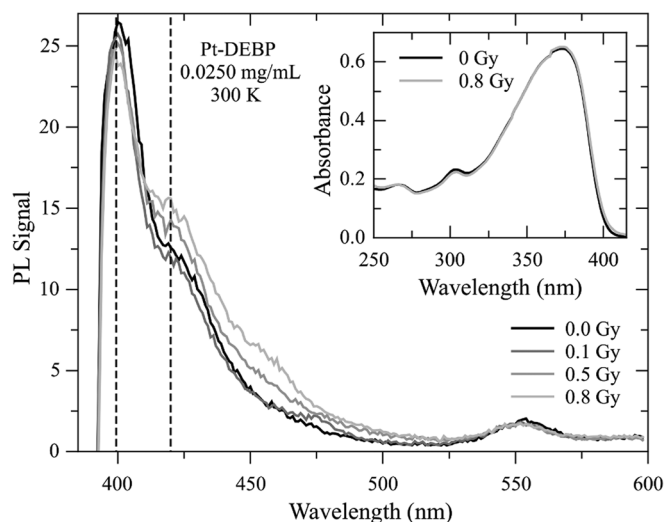


FIG. 1. Photoluminescence spectra of the solutions irradiated at doses below 1 Gy. The insert shows the absorbance of the solutions before and after irradiation with 0.8 Gy.

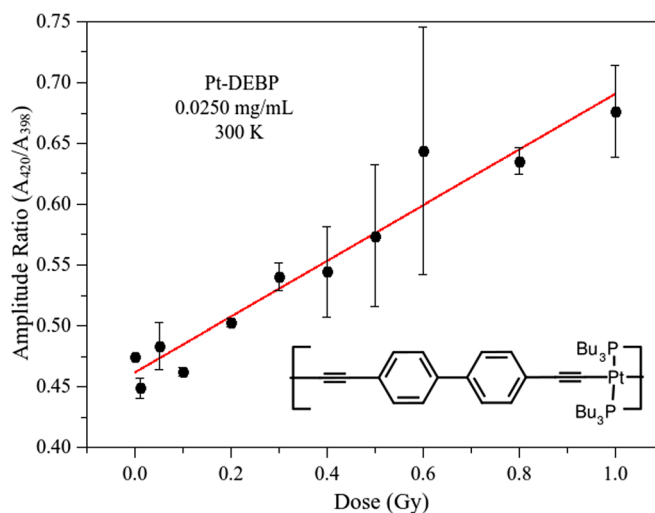


FIG. 2. Ratio of the emission peak at 420 nm with respect to the main peak at 398 nm (A_{420}/A_{398}) as a function of dose for solutions of 0.025 mg/ml and Pt-DEBP monomer structure.

Similar results were obtained in all concentrations used. Fig. 2 shows the dependence of the amplitude ratio of the emission peak at 420 nm with respect to the main peak at 398 nm (A_{420}/A_{398}), as a function of dose for a concentration of 0.0250 mg/mL.

In order to evaluate the use of these solutions as dosimeters, changes in the spectrum after storage were also monitored. Fig. 3 shows the A_{420}/A_{398} for different doses, while the inset shows the emission spectrum, after 1 and 4 months of storage, for a concentration of 0.0250 mg/mL.

As can be seen from Fig. 3, there are small changes in the main peak position for samples stored for 30 days; however, after 120 days of storage A_{420}/A_{398} becomes dose independent. Notice that in the inset of Fig. 3, after 120 days a new emission band at 445 nm is observed regardless of the dose applied.

In general, the emission spectrum of organometallic systems like Pt-DEBP is a result of several competing emissive and non-emissive transitions, e.g., metal-ligand (MLCT) or intra-ligand charge transfer (ILCT), so it is greatly influenced by structural changes in the ligands.¹⁸⁻²² Moreover, it is

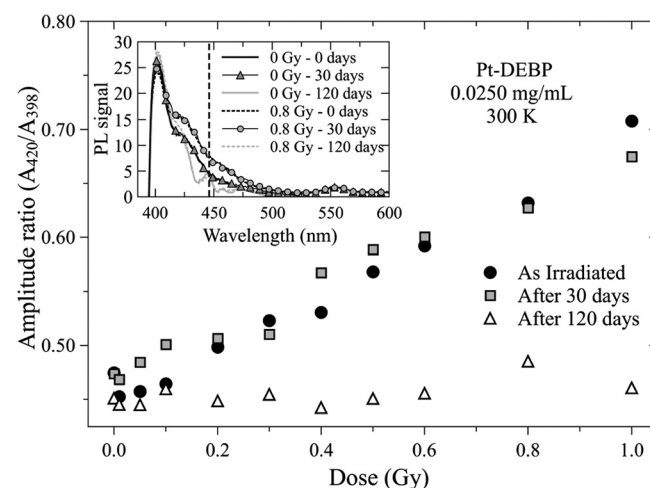


FIG. 3. Amplitude ratio for different doses with storage time, for a concentration of 0.0250 mg/mL. The inset shows the emission spectrum, after 1 and 4 months of storage.

known that square planar Pt complexes can interact through π - π or Pt-Pt interactions, promoting aggregates and thus excimer formation that result in significant changes in the emissive states of the compound in solution.^{21–25} These interactions are very sensitive to changes in the chemical environment such as temperature, concentration, solvation, pH, presence and nature of counter ion, and variations in covalent interactions.^{24–26} In this sense, it is very difficult to address the exact origin of the changes observed in Fig. 1.

In our previous studies, it was shown that the structural changes in Pt-DEBP after irradiation are due to: (i) incorporation of radical chlorine mainly on the triple bonds and (ii) polymer chain increase.^{11,12} These changes are followed by significant changes in the absorption spectrum of the system for doses between 1 and 90 Gy. Considering the mechanism proposed,¹² the absence of significant shifts in the absorption spectrum, see the inset of Fig. 1, suggests that the amount of radical incorporation at low doses is very small. In addition, it also indicates that the effect in the emission spectrum is related to modifications in the vicinity of the metal center and alkynyl ligands rather than to changes in the conjugated segment. Thus, one possible origin of the new band at 420 nm is associated to changes in π - π^* transition from (-C \equiv C-R) IL/ $d\pi$ (M)- π^* (-C \equiv C-R) MLCT triplet state with predominantly IL character.^{22–26} In fact, the incorporation of electron withdrawing groups like chlorine can reduce the spin density on the metal, promoting an increase of the quantum efficiency of the fluorescence and a blue-shift in the UV-Vis spectra, observed at high doses. Similar effects are also expected, when the polymer chain is increased.^{12,19} Thus, the effect observed in the emission spectrum could be understood based on the mechanism proposed.¹²

However, a more detailed description deserves more research. Despite this, it is clear from Fig. 1 that Pt-DEBP/CHCl₃ solutions respond to doses below 1 Gy, which is not the case for MEH-PPV.¹²

A desirable characteristic of a dosimeter is to have a constant sensitivity across the range of measured dose. This constant dose sensitivity is reflected in a linear response of the measured quantity on dose, as can be seen in Fig. 2. In this particular case, the linear response can be written as $A_{420}/A_{398} = (0.462 \pm 0.019) + (0.229 \pm 0.019)D$ with $R^2 = 0.94$; where A_{420}/A_{398} represents the ratio between the emission signal amplitudes at 420 and 398 nm; D represents the applied dose; and R^2 the square of the linear correlation parameter. By considering the angular coefficient of the proposed equation, a sensitivity of $0.229 \pm 0.019 \text{ Gy}^{-1}$ is obtained.²⁷ Another important dosimetric parameter to be evaluated is the inferior limit of detection (IDL), defined as the minimum dose observable. It can be evaluated from the emission spectrum of the non-irradiated samples by considering $IDL = (DQ_0 + 3\sigma_{DQ(0)})/f$,²⁷ where DQ_0 is the average of A_{420}/A_{398} for non-irradiated solutions; $\sigma_{DQ(0)}$ is the standard deviation, and f is the angular coefficient of the linear fit. Using this procedure, an IDL of 0.106 Gy is obtained. Furthermore, samples were irradiated in duplicate (data not shown) in order to evaluate the repetitibility of the measurements. A small variation was observed (less than 1%), between different set of samples. Thus, our dosimeter has a constant high sensitivity, with high accuracy.

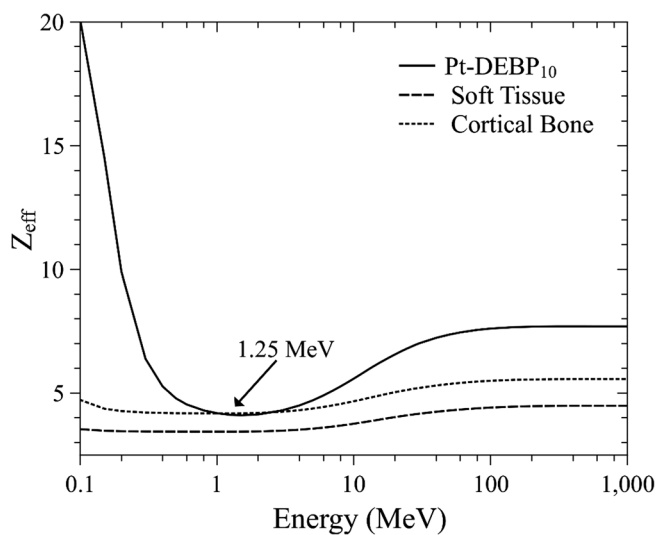


FIG. 4. Comparison of the estimated Z_{eff} obtained for Pt-DEBP₁₀ and typical human tissues.

Stability is another important parameter to evaluate in a dosimeter. Fig. 3 shows that the dosimeter can be stored for 30 days. Note that after 120 days, a new emission band is observed at 445 nm. This is a feature commonly observed in square planar Pt(II) complexes solutions.^{23–28} Polymer in solutions exhibits non-covalent interactions such as hydrogen bonding, which is one of the most important driving forces in supra-molecular aggregation. Since this band appears independent on gamma ray irradiation, we attribute it to aggregation. Thus, the results indicate that Pt-DEBP/CHCl₃ has good stability when stored up to at least 30 days.

In order to better evaluate the possibility of using these systems for medical applications, another relevant parameter to be considered is the effective atomic number (Z_{eff}).²⁹ Fig. 4 shows the comparison of the estimated Z_{eff} obtained for Pt-DEBP₁₀ and typical human tissues by employing the approach described by Taylor *et al.*³⁰

As can be seen, for the typical energy of ⁶⁰Co γ -rays ($\sim 1.25 \text{ eV}$), the system Pt-DEBP₁₀ presents Z_{eff} values between soft tissues and cortical bones of the human body, attesting its applicability in personal dosimetry. Finally, regarding the applicability of the evaluated system as dosimeter, it is important to mention that due to the irreversibility of the reactions involved, it is impossible to reset the system after irradiation hindering its reutilization. However, the dosimeter accumulates the doses absorbed; thus, it can be used, for example, in personal dosimetry. After its use, it can be discarded. Remember that the cost estimate for this dosimeter is very low, around 1 US\$ maximum.

In summary, Pt-DEBP/CHCl₃ is a promising dosimeter for doses below 1 Gy. Using the ratio of PL emission bands at 420 nm and 398 nm, a linear response with dose in the range of 0.1 to 1 Gy is observed. The method is robust and can be used on any fluorimeter. The dosimeter has high sensitivity, accuracy and can be stored for up to 30 days.

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