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# $CdWO_4$-on-MEH-PPV:PS as a candidate for real-time dosimeters

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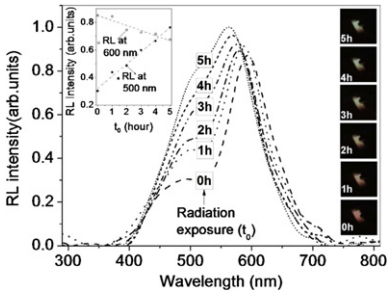
## HIGHLIGHTS

- Thin composite film dosimeters using a combination of a scintillator crystal and a light-emitting polymer.
- A X-ray dose detector based on MEH-PPV/$CdWO_4$ materials which are rarely seen together.
- A new smart, disposable and easy-to-read organic–inorganic radiation detector.

## GRAPHICAL ABSTRACT

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## ABSTRACT

We report on the investigations about the modification of optical properties induced by X-rays onto film detectors of cadmium tungstate ($CdWO_4$), poly[2-methoxy-5(2′-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV) and polystyrene (PS) This device takes advantage of reduction of spectral overlap between the radioluminescence (RL) of $CdWO_4$ and the absorption of MEH-PPV as it is exposed to radiation, forming the basis of a new dosimeter that is capable of converting the orange-red radioluminescence of PS:MEH-PPV:$CdWO_4$ into green. We propose an explanation of the optical processes occurring in MEH-PPV:$CdWO_4$ in terms of the radiation hardness of $CdWO_4$ combined to the RL-induced degradation of MEH-PPV.



## 1. Introduction

Recent advances in new and highly complex treatment modalities using ionizing radiation have initiated a demand for new methods of dosimetry and imaging systems [1–3]. Substantial progress in the field of scintillator materials observed in the last decades was made possible by both the development of new materials and the efforts focusing the efficient manufacturing of easy-to-read and easy-to-use radiation sensors [4]. This is the case of cadmium tungstate ($CdWO_4$) [5], which has been developed for applications in detectors for radiometry, registering gamma-radiation and X-ray scanners. The most remarkable features of this material are its high radioluminescence (RL) of $2 \times 10^4$ photons $MeV^{-1}$ at about 500 nm, and also its radiation hardness when compared with other inorganic scintillators [6,7]. It means that $CdWO_4$ presents blue light emission that is reproducible even after high doses of X-rays or gamma radiation. Nevertheless, this scintillator can also be employed in photonic devices exploring radiation damage, if combined with the convenient organic material. An additional advantage of this hybrid system for the medical markets would be the possibility to produce large sheets of $CdWO_4$-on-polymer devices. The solution-based thin film deposition technology is attractive for achieving processability of

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an inexpensive, chemically inert and optically transparent thermoplastic, such as the polystyrene (PS), with the functional optical performance and properties of a conventional–radiation-stable scintillation material. This allows processing of flexible thin films detectors with speed and efficiency at low-cost. To sustain the viability of the proposed device, a key requirement is the ability to process the $CdWO_4$ dispersed in organic matrixes. Keeping in mind that organic matrixes can also be obtained from light-emitting polymers (LEPs) films which are relatively stable under X-rays [8–11], but unstable under visible illumination. Particularly, LEPs undergo a blue-shift and a reduction of their luminescence when exposed to blue-light (450–460 nm) [12,13], such as the RL of $CdWO_4$ [5]. A real-time hybrid dosimeter may be achieved by mixing $CdWO_4$ with PS and few amounts of LEPs. The luminescence of this hybrid system may present blue-shift as it is exposed to X-rays, forming the basis of a color-indicator dosimeter if the proper care is taken with calibration conditions. This system is of prominent interest in current development and applications on dosimetry. In order to bring out specific issues concerning this idea, we will consider the influence of irradiation on the color variation of $CdWO_4$:LEP system during the irradiation process. In fact, the purpose of the work reported here is to study the influence of X-rays on the emission color of flexible, easy-to-read and easy-to-use thin composite film dosimeters using a combination of a scintillator crystal and a LEP that form a new hybrid system which are not usually seen together.

## 2. Experimental

Cadmium tungstate $CdWO_4$ powder was obtained as described elsewhere [5], while poly (2-methoxy-5(2′-ethylhexyloxy)-*p*-phenylenevinylene) – MEH-PPV, a red-orange luminescent LEP, was purchased from Aldrich–Sigma, and the chemically inert PS from Innova-Petrobras. PS:MEH-PPV = $1/10^{-3}$ (wt/wt), PS:$CdWO_4$ = 1/0.4 (wt/wt) and PS:MEH-PPV:$CdWO_4$ = $1/10^{-3}$/0.4 (wt/wt/wt) were dissolved in chloroform. PS:MEH-PPV, PS:$CdWO_4$ and PS:MEH-PPV:$CdWO_4$ films were prepared by the solvent-casting method onto glass substrates at 300 K, which is above the glass transition ($T_g$) of PS [14] and MEH-PPV [15] to produce samples with a well-defined and reproducible thermal history. Flexible and free-standing films of 150 μm thicknesses were removed from glass substrate with the aid of a spatula. UV–vis absorption (ABS) and photoluminescence (PL) spectra of PS:MEH-PPV were carried out in the 300–800 nm range using the Shimadzu UV 1650 equipment with a blue-LED (peak at about 465 nm, 3 mm, 1500 mcd) as the excitation source and the ISS PC1 Spectrofluorimeter, respectively. The radioluminescence (RL) spectra of PS:$CdWO_4$ and PS:$CdWO_4$:MEH-PPV were acquired using an Ocean Optics HR 2000 spectrometer (resolution of 0.5 nm), while the samples were under excitation of X-rays emitted by a Cu target tube operating at 40 kV/40 mA. At this configuration, the dose rate was estimated using an ion chamber (Radcal corporation model 2025 radiation monitor) as ~3 Gy $min^{-1}$. All measurements were performed in the dark and at room temperature to prevent photo and thermal degradation processes.

## 3. Results and discussion

The optical response of PS:MEH-PPV, PS:$CdWO_4$ and PS:MEH-PPV:$CdWO_4$ films are shown in Fig. 1. The main ABS and PL bands of PS:MEH-PPV were observed to occur at 475 nm and 605 nm, respectively. The RL band of PS:$CdWO_4$ occur at 495 nm, while the emission maxima from PS:MEH-PPV:$CdWO_4$ can be observed at 490 nm and 590 nm, respectively. This figure demonstrates that both PL of MEH-PPV and RL of $CdWO_4$ spectra are included in the

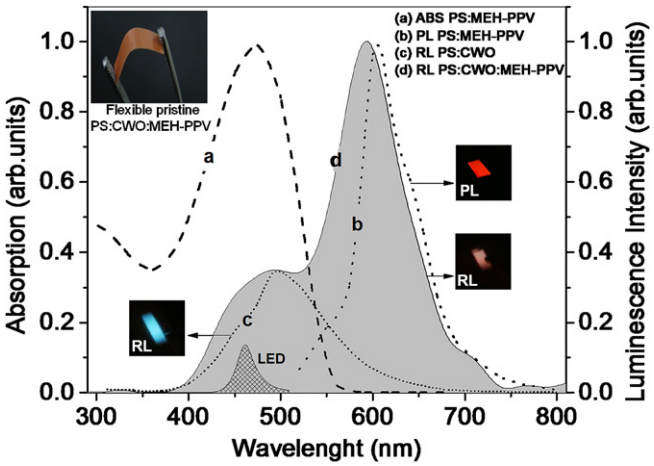


**Fig. 1.** Optical response of PS:MEH-PPV, PS:$CdWO_4$ and PS:MEH-PPV:$CdWO_4$ pristine films. (a) ABS of PS:MEH-PPV, (b) PL of PS:MEH-PPV, (c) RL of PS:$CdWO_4$ and (d) RL of PS:MEH-PPV:$CdWO_4$. The spectrum of the blue-LED used as excitation source for PL measurements was also shown in this figure. The inset presents a photograph of a flexible pristine PS:$CdWO_4$:MEH-PPV film.

PS:MEH-PPV:$CdWO_4$ emission spectrum. Additionally, one can observe that the RL emission band of $CdWO_4$ is overlapped by the MEH-PPV absorption with improved PL intensity of MEH-PPV. This result is consistent with a resonance energy transfer from the inorganic material to the luminescent polymer [16,17]. This topic is deferred for future work. In addition, the interaction of X-rays with $CdWO_4$ occurs mainly through photoelectric effect. The electrons and holes released in this process migrate through the material promoting further ionizations until they lose energy and are thermalized in the conduction and valence band, respectively. Electronic structure calculations of $CdWO_4$ have shown that O 2*p* states dominate the top of the valence band whereas the bottom of the conduction band derive primarily from W 5*d* states [18]. Radioactive recombination of these electrons and holes occurs, with the energy being successfully transferred to tungstate group responsible for the emission in the blue region of visible spectrum. At PS:MEH-PPV:$CdWO_4$, a resonant energy transfer between scintillator and polymer during X-rays excitation can be hypothesized, since the MEH-PPV absorption spectrum overlaps the $CdWO_4$ emission band and the luminescence of the samples presents a remarkable band at 500–750 nm, which is related to MEH-PPV emission.

Fig. 2 presents the effect of radiation dose ($t_0$) delivered by the X-ray source on the variation of RL and color of PS:MEH-PPV:$CdWO_4$. One must notice that after 5 h of X-ray exposition, the total dose deposited on the film is approximately 900 Gy. It can be seen from the RL spectra that for higher values of $t_0$, the RL peaks of PS:MEH-PPV:$CdWO_4$ shift towards lower wavelengths (blue-shift), and we observe a slight increase of the RL intensity at 600 nm and a strong increase at 500 nm due to the radiation exposure (*i.e* 5 h). Consequently, the color emission changes from orange-red to green. On the other hand, the RL spectra of PS:MEH-PPV film is relatively stable over the same radiation exposure, and this result is consistent with that of Ref. [3]. As suggested by the previous work of some of the authors on the effect of ionizing and non-ionizing radiation of conjugated polymer [3,19], we assume that the blue shift in the RL spectra of PS:MEH-PPV:$CdWO_4$ results from the decrease of the effective conjugation length of MEH-PPV and the reduction of spectral overlap between the blue-emission of $CdWO_4$ and the absorption of MEH-PPV. It is consistent with the replacement of vinyl group by carbonyl groups on MEH-PPV backbone mainly because of degradation processes induced by photooxidation

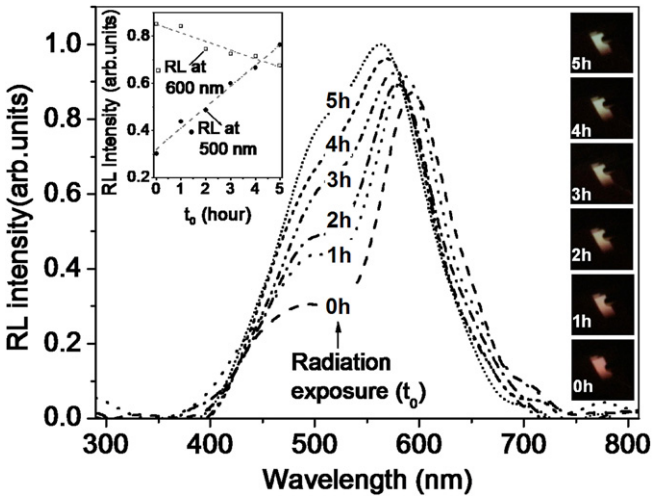


**Fig. 2.** Radioluminescence (RL) spectra obtained from PS:MEH-PPV:$CdWO_4$ films exposure to X-ray during 5 h. All measurements were performed at room temperature. The inset displays the evolution of RL intensity at 500 nm and 600 nm as function of radiation exposure (the lines are only guiding for the eyes).

process. This is consistent with Refs. [12,13]. In fact, these results support the idea of a novel disposable and real-time monitor organic–inorganic device for X-ray.

In order to obtain the linearity of the radiation detector, we considered the wavelengths of the most intense emission at 500 nm from PS:$CdWO_4$ and at 600 nm from PS:MEH-PPV on the RL of PS:MEH-PPV:$CdWO_4$ spectra, as reasonably practical parameters (inset of Fig. 2). Both RL at 500 nm and at 600 nm intensities show linear radiation-time dependences (full lines). The percentage error was near 10% and 2% for RL at 500 nm and 600 nm, respectively.

## 4. Conclusions

In summary, the results reported here clearly demonstrate the feasibility of using $CdWO_4$-on-luminescent polymer materials for X-ray dosimeters. It is therefore concluded that PS:MEH-PPV:$CdWO_4$ films appear as good candidates for indicator detector that offers an optical real-time and read-out. These indicators are significantly easier to monitor than a conventional dosimeter, which requires a spectroscopic measurement to determine the dose absorbed. The results obtained, which to our knowledge are new for flexible X-ray dosimeters, have enabled a quantitative analysis to be made of how the RL of PS:MEH-PPV:$CdWO_4$ films is strongly affected with the radiation-induced degradation of MEH-PPV and an efficient spectral overlap between the absorption of photo-oxidized MEH-PPV and the radioluminescence of $CdWO_4$. Advantages of the use of the $CdWO_4$-on-MEH-PPV system as single-used disposable device are low cost, easy preparation of samples and simplicity for dose evaluation. Future work should concentrate on enhancing the performance of the device, but we are confident that our research will serve as a base for future studies on flexible real-time dosimeters for ionizing radiation.

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