



Technical note

X-rays sensing properties of MEH-PPV, Alq₃ and additive components: A new organic dosimeter as a candidate for minimizing the risk of accidents of patients undergoing radiation oncology

T. Schimitberger^a, G.R. Ferreira^a, L.C. Akcelrud^b, M.F. Saraiva^c, R.F. Bianchi^{a,*,1}

^a Laboratory of Polymers and Electronic Properties of Materials, UFOP, Ouro Preto, MG, Brazil

^b Laboratory of Polymers Paulo Scarpa, UFPR, Curitiba, PR, Brazil

^c Radiotherapy Center of Cristiano Varella Foundation, Muriaé, MG, Brazil

ARTICLE INFO

Article history:

Received 21 December 2011

Received in revised form 30 July 2012

Accepted 7 August 2012

Keywords:

Radiotherapy

Polymer

Organic device

Organic electronic

Dosimeter

Smart sensor

ABSTRACT

In this paper, we report our experimental design in searching a smart and easy-to-read dosimeter used to detect 6 MV X-rays for improving patient safety in radiation oncology. The device was based on an organic emissive solutions of poly(2-methoxy-5(2'-ethylhexyloxy)-*p*-phenylenevinylene) (MEH-PPV), aluminum-tris-(8-hydroxyquinoline) (Alq₃) and additive components which were characterized by UV-Vis absorption, photoluminescence and CIE color coordinate diagram. The optical properties of MEH-PPV/Alq₃ solutions have been examined as function of radiation dose over the range of 0–100 Gy. It has shown that MEH-PPV/Alq₃ solutions are specifically sensitive to X-rays, since the effect of radiation on this organic system is strongly correlated with the efficient spectral overlap between Alq₃ emission and the absorption of degraded MEH-PPV, which alters the color and photoemission of MEH-PPV/Alq₃ mixtures from red to yellow, and then to green. The rate of this change is more sensitive when MEH-PPV/Alq₃ is irradiated in the presence of benzoyl peroxide than when in the presence of hindered phenolic stabilizers, respectively, an accelerator and an inhibitor to activate or inhibit free radical formation. This gives rise to optimize the response curve of the dosimeter. It is clear from the experimental results that organic emissive semiconductors have potential to be used as dedicated and low-cost dosimeters to provide an independent check of beam output of a linear accelerator and therefore to give patients the opportunity to have information on the dose prescription or equipment-related problems a few minutes before being exposed to radiation.

© 2012 IPEM. Published by Elsevier Ltd. All rights reserved.

1. Introduction

The fatal radiation overdose of cancer patients under radiation therapy has become a recent focus of provocative headlines and concern of hospitals, healthcare organizations, professionals in radiation oncology and institutions for improving patient safety [1–3]. This issue was followed by investigations from the American Association of Physicists in Medicine and American Society of Radiation Oncology, which have been summarized in recent article [4]. In view of the several recommendations presented in this paper to avoid equipment malfunctions and human mistakes, it now seems to be an appropriate time to propose innovative solutions

for indication of dose radiation delivered to cancer patients shortly before being exposed to radiation therapy treatment. This way they will have the assurance that the prescribed dose for their cancer treatment will be administered correctly. Unfortunately, errors are common in radiation therapy and to establish medical and hospital routines to prevent negative impacts on the treatment of patients with cancer are a current challenge [4–7]. Some of the difficulties in establishing new routines are associated with the complexity of cancer treatments and also to tighter control of the operating conditions of hospital equipment prior to patient exposure to radiation. Therefore, investments in new technologies can ensure safe and effective treatments to cancer patients not only because it will inform that equipments are working properly, but also that such information can be obtained and delivered to the patients, and thus are not putting them at risk. Accordingly, these investments will contribute to ensure that cancer patients will be treated with respect, support and security in agreement with the general conclusions of Ref. [4].

This paper reports the experimental design of a personal real-time radiation detector for 6 MV X-rays for improving patient safety

* Corresponding author at: UFOP, 35400000 Ouro Preto, MG, Brazil.
Tel.: +55 31 35591742.

E-mail addresses: bianchi@iceb.ufop.br,
bianchi@eecs.berkeley.edu (R.F. Bianchi).

¹ Presently, he is a Visiting Scientist at Department of Electrical Engineering and Computer Sciences, UC Berkeley - USA.

in radiation oncology. Our main goal is to find and evaluate a new system with potential use as an easy-to-read dose indicator radiation detector which should necessarily be inexpensive and thus accessible in places with limited resources. Firstly, we will consider the effect of irradiation on the optical properties of light-emitting polymers (LEPs) [8–12], which can be easily detected by irreversible color variation of such organic materials during the irradiation process [12–15]. The simple correlation between dose and color is the main feature of the proposed device. In fact, the phenomenon of color variation induced by radiation not only reveals the irreversible changes that can occur on the optical properties of LEPs during radiation therapy treatments, but also provides a real-time independent verification and convenient probe for monitoring radiation doses delivered by external beam radiation machine or equipment-related problems, such as radiation underdose and overdose.

2. Experimental procedures

Poly(2-methoxy-5(2'-ethylhexyloxy)-*p*-phenylenevinylene) – MEH-PPV and [aluminum-tris-(8-hydroxyquinoline)] – Alq₃ were purchased from Aldrich Sigma and dissolved in chloroform at a MEH-PPV/Alq₃ (w/w) ratio equal to 0.5 as described elsewhere [14,15]. MEH-PPV/Alq₃ was also dissolved in chloroform containing benzoyl peroxide (from Aldrich Sigma) and hindered phenolic stabilizers (Irganox 1010®, from Ciba Specialty Chemical Corporation), an accelerator and an inhibitor of radical formations, respectively. The additives were used to enhance the stability of MEH-PPV by a hindered phenol as well to reduce it by peroxides [16,17], and no significant differences in the line shape of ABS and PL curves of MEH-PPV/Alq₃ solutions were observed with the presence of these additives. These solutions will be described as MEH-PPV/Alq₃:accelerator and MEH-PPV/Alq₃:inhibitor. In fact, the samples were prepared in the dark to avoid light-induced degradation of the organic systems, and molecular sieves were added to chloroform to remove the traces of water. Although no systematic study of the effect of oxygen, moisture or daylight was undertaken, no visible change was noticed on the pristine samples that stood exposed to daylight on the laboratory for several days. Finally, the solutions were transferred to glass ampoules which were then flame-sealed to avoid solvent evaporation. The specifications for ampoules were: nominal volume, diameter, external thickness and wall thickness of 1.25 ml, 10 mm, 8.0 mm and 0.50 mm, respectively. The irradiation of the samples by X-rays was performed at the Radiotherapy Center of *Fundação Cristiano Varella* – Brazil to evaluate the effect of ionizing radiation in the range of 0–100 Gy on the optical properties of MEH-PPV/Alq₃ hybrid material. In the present study, Varian Clinac 600C LINAC computer-controlled equipment with a conventional X-rays source was used. This machine generates a 6 MV X-rays beam with rectangular symmetric fields [18] and delivers the exact prescribed dose to the patient in the lowest number of monitor units. The irradiation of samples was performed in a water phantom according to IAEA TRS 398 dosimetry protocols [19] at a source-surface distance of 100 cm with a (30 cm × 30 cm) field in order to simulate the standard conditions of cancer treatment. The photoemission (PL) spectra of MEH-PPV/Alq₃ systems was recorded using an USB2000 Ocean Optics spectrophotometer, with an InGaN laser ($\lambda = 405$ nm, 10 mW) as excitation source. Finally, UV–Vis absorption spectra were carried out in the 300–800 nm range using the Shimadzu UV 1650 equipment, and the color coordinates of CIE (1931) chromaticity diagram were obtained using the PL spectra of organic solutions and the Color Calculator Free Software. All measurements were done at room temperature.

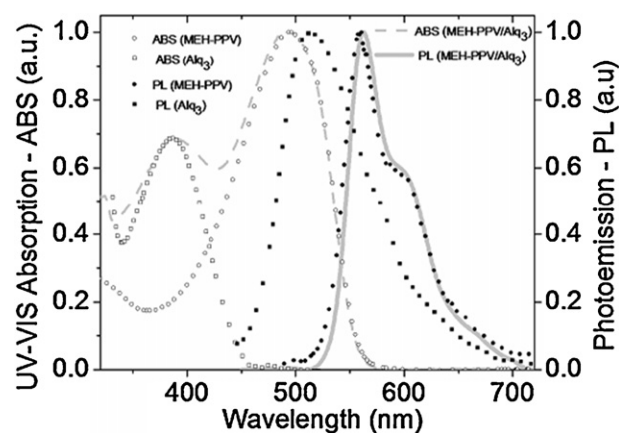


Fig. 1. UV–Vis absorption (ABS) and photoemission (PL) spectra obtained from MEH-PPV, Alq₃, and MEH-PPV/Alq₃ solutions. All measurements were performed at room temperature. The PL spectra were recorded on the USB2000 spectrophotometer with a 405 nm laser as excitation source.

3. Experimental results

The optical response of MEH-PPV, Alq₃ and MEH-PPV/Alq₃ solutions are shown in Fig. 1. The main peaks were observed to occur at 495 nm and 385 nm for absorption (ABS), and at 560 nm and 515 nm for photoluminescence (PL) for MEH-PPV and Alq₃, respectively. A single PL peak at 560 nm and two distinct absorption peaks at 385 nm and 492 nm were observed for MEH-PPV/Alq₃. This figure represents a control experiment which demonstrates that both MEH-PPV and Alq₃ absorption spectra are observed to occur in the MEH-PPV/Alq₃ hybrid material, while the PL of Alq₃ is reabsorbed by the MEH-PPV. This finding indicates that an energy transfer process from Alq₃ to MEH-PPV is taking place, since a large spectral overlap between Alq₃ emission and MEH-PPV absorption is observed. This is in agreement with reported results [20] describing the influence of small-molecule material on the performance of MEH-PPV-based solar cells indicating a probability of Förster energy transfer from Alq₃ to MEH-PPV.

3.1. Influence of 6 MV dose levels on the optical properties of MEH-PPV/Alq₃ hybrid material

It can be seen from Fig. 1 that there exists a red-orange emission band between 520 nm and 690 nm for both MEH-PPV and MEH-PPV/Alq₃ solutions. Let us assume the Förster energy transfer from Alq₃ to MEH-PPV and also the instability to radiation of substituted poly(phenylenevinylene) – PPV [21–23]. Bearing these points in mind, it seems to be reasonable to expect a quenching of the PL intensity due to the decrease of the polymer conjugation length under exposure to radiation [21,23,24], and thus a less effective spectral overlap between the absorption of MEH-PPV and the emission of Alq₃.

The findings outlined above have been applied to the design of a novel smart organic detector of X-rays (6 MV) using MEH-PPV/Alq₃-based material. We illustrate this by considering the design of an X-rays dose indicator showing color variation from red to yellow, and then to green when exposed to doses in the range of 0–100 Gy. In Fig. 2 is displayed the effect of radiation on both the optical properties (ABS and PL) of MEH-PPV/Alq₃ solution. It is observed that the MEH-PPV absorption (370–560 nm) and red-orange emission (520–690 nm) bands shift towards lower wavelengths and decrease in intensity with dose levels, while the Alq₃ absorption (300–450 nm) and green emission (450–650 nm) bands remain constant with substantial increases in intensity, respectively. An inset to Fig. 2 shows the linearity of the peak

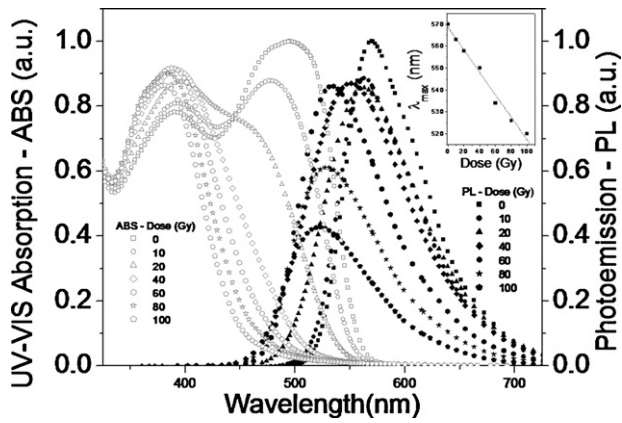


Fig. 2. UV-Vis absorption (ABS) and photoemission (PL) spectra obtained from MEH-PPV/Alq₃ solutions exposure to 6 MV X-rays doses equal to 0, 10, 20, 40, 60, 80 and 100 Gy. All measurements were performed at room temperature. The PL spectra were recorded on the USB2000 spectrophotometer with a 405 nm laser as excitation source. Inset: peak emission wavelength (λ_{\max}) of MEH-PPV/Alq₃ solutions exposed to X-rays doses.

emission wavelength (λ_{\max}) vs. dose of MEH-PPV/Alq₃ solution. From these experimental results, it is shown that a blend of the two luminescent organic materials in solution therefore undergoes a blue-shift in PL emission and absorption as they are exposed to radiation, forming the basis if a linear-response dosimeter for radiation oncology.

3.2. Influence of 6 MV dose levels, benzoyl peroxide and of hindered phenolic stabilizers on performance of MEH-PPV/Alq₃-based detector

Figs. 3 and 4 show the radiation dose evaluation to MEH-PPV/Alq₃:inhibitor, MEH-PPV/Alq₃ and MEH-PPV/Alq₃:accelerator solutions. The irradiation used was 6 MV X-rays, and the results were obtained from direct measurement on the CIE (1931)

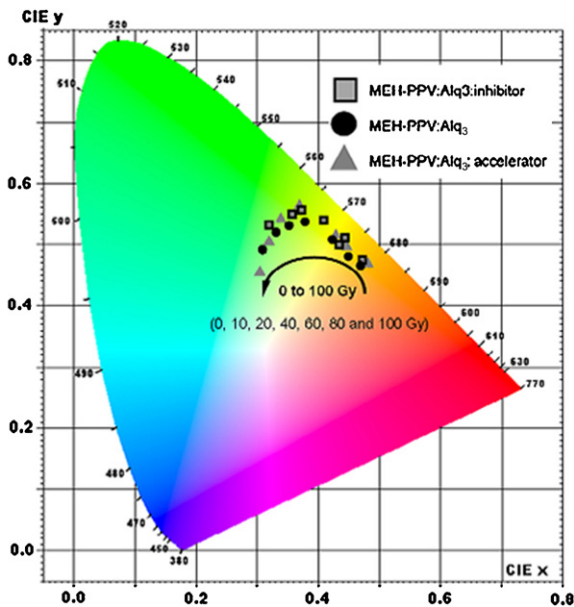


Fig. 3. CIE (1931) chromaticity diagram obtained from MEH-PPV/Alq₃:inhibitor, MEH-PPV/Alq₃ and MEH-PPV/Alq₃:accelerator solutions exposure to 6 MV X-rays doses equal to 0, 10, 20, 40, 60, 80 and 100 Gy. The diagrams were obtained using the PL spectra showed in Fig. 2 and the Radiant Imaging Color Calculator Free Software. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

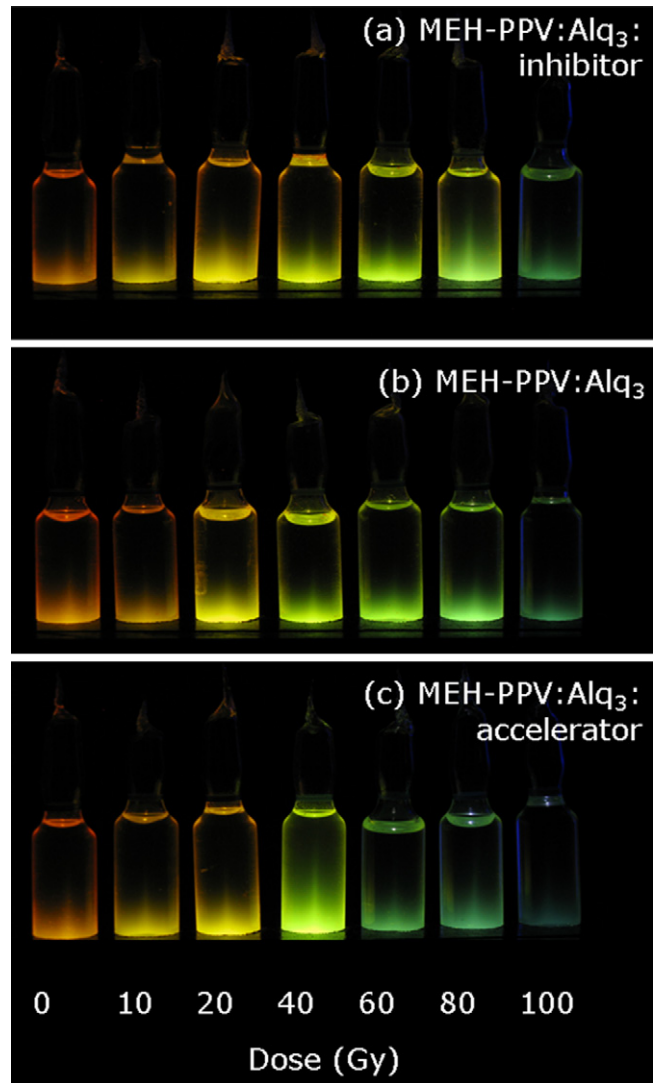


Fig. 4. Set of 7 sealed glass ampoules filled with (a) MEH-PPV/Alq₃:inhibitor, (b) MEH-PPV/Alq₃ and (c) MEH-PPV/Alq₃:accelerator solutions obtained from exposure to 6 MV X-rays doses equal to 0, 10, 20, 40, 60, 80 and 100 Gy. All the organic materials were excited by a violet light (emitted from a violet LED with wavelength from 380 to 410 nm). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

chromaticity diagram and on the pictures of a set of seven excited organic samples exposed to 0, 10, 20, 40, 60, 80 and 100 Gy. All samples were mounted in a specially constructed sample holder and excited with a violet LED (380–410 nm) at an oblique angle. The dosimeters emission changed from red to green when the dose rises above 40 Gy for MEH-PPV/Alq₃:accelerator, and above 60 Gy for MEH-PPV/Alq₃ and MEH-PPV/Alq₃:inhibitor. With further increases in dose rate, Fig. 5 shows the peak emission wavelength (λ_{\max}) MEH-PPV/Alq₃:inhibitor, MEH-PPV/Alq₃ and MEH-PPV/Alq₃:accelerator changed linearity from green to greenish blue when dose reached 60, 80 and 100 Gy, respectively. The color of the organic solutions does not change back after exposure to radiation. In fact, a set of 21 samples, all three of them were irradiated with the same dose (0, 10, 20, 40, 60, 80 and 100 Gy) showed a very similar color-changing response. This procedure guaranteed reproducibility in the preparation processes, and also the high optical performance of the organic solutions.

It can be seen from Figs. 3–5 that addition of benzoyl peroxide (accelerator) has enhanced degradation process of MEH-PPV, while the addition of hindered phenolic stabilizers (inhibitor), on the

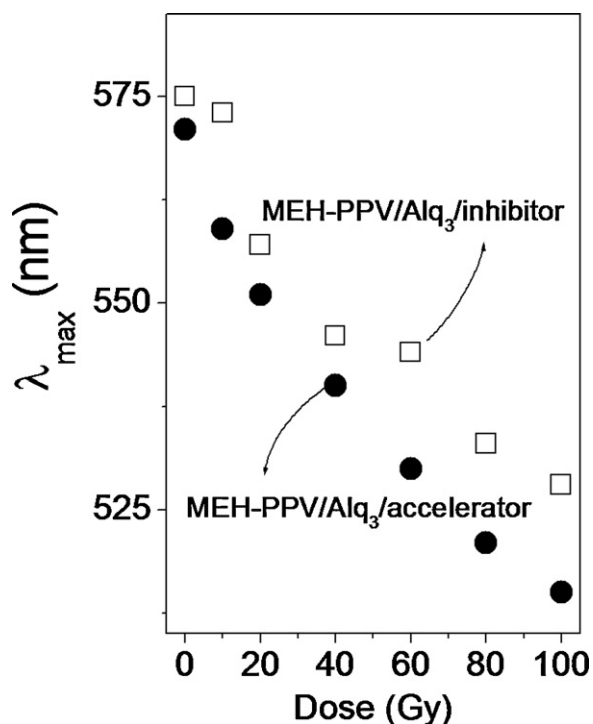


Fig. 5. Peak emission wavelength (λ_{\max}) vs. dose obtained from MEH-PPV/Alq₃:inhibitor and MEH-PPV/Alq₃:accelerator solutions exposed to X-rays doses.

other hand, has retarded. It is clear from these experimental data that a reasonably self-consistent picture has emerged regarding the basic degradation process of MEH-PPV enhanced by hindered phenolic stabilizers and reduced by benzoyl peroxide. Our findings would seem to demonstrate that the radiation exposure promotes changes in the absorption and photoluminescence spectra of PPV-type polymers that point towards the idea of chain scission and decrease of conjugation length. This effect is attributed to radical transfer reaction from the polymer backbone to the added compound, where it is stabilized by resonance in the rings. Consequently, the slowdown of the photo degradation by the presence of the free radical scavenger indicates that free radicals act as an accelerator of the photo-oxidation process. However, despite this effort, there are still uncertainties associated with role of these compounds on the degradation process of PPV-type polymers, thus becoming a significant subject of study for future publications [17].

4. Conclusions

In this paper, we have reported the results of an investigation on the use of a small molecule/light-emitting polymer hybrid material to produce a new radiation dosimeter for minimizing the risk of accidents of patients undergoing radiation oncology. Device operating principle is based on changing the effective spectral overlap between the absorption of MEH-PPV and the emission of Alq₃ solutions during irradiation process. This principle was chosen from reasons of the instability to radiation of MEH-PPV, and the possibility of controlling the degradation rate of this PPV-type polymer by adding free radicals scavengers or delivering compounds. The results presented demonstrated that MEH-PPV/Alq₃ devices can successfully be programmed to operate from 0 to 100 Gy. The basic idea behind this concept considers the sensor as a novel *organic luminescence traffic light device* in which red represents, for example, underdose and green the prescribed dose, while orange-yellow suggests that radiation therapy procedure is an ongoing process

and greenish blue, overdose. One of the benefits often pointed out in connection with Ref. [4] is that the MEH-PPV/Alq₃ dosimeter has the capability of easily providing the radiation dose shortly before the radiation treatment of cancer patients to avoid fatal overdose or underdose, because the majority of tumors require doses in the range of 8–70 Gy, which are fractionated in doses of 1.8–2.0 Gy once a day, five times a week for 5–7 weeks. The conclusion to be drawn from all the work in searching a smart and easy-to-read dosimeter is that, although the sensitivity, performance and reproducibility MEH-PPV/Alq₃-based dosimeter have not yet been explored, the results presented demonstrate that: (i) small molecule-light/emitting polymer hybrid material can successfully applied as a disposable, personal and very low-cost (<US\$ 1) X-rays detector for minimizing errors in the application of medical radiation, such as miscalibration of a LINAC income unit resulting in incorrect treatment dose, and to give patients the opportunity to have information on the dose calibration, equipment-related problems and system faults a few minutes before being exposed to radiation, and (ii) the monitoring of this device may also be easily achieved, for example, by establishing calibration conditions for colors obtained by passing the radiation through the organic system. A check against a standardized color chart can easily supply the delivered dose.

Acknowledgments

This research was supported by the CNPq (grant numbers 305646/2010-9 and PDE 200682/2011-3), by Rede Nanobiomed/Capes, by CNPq-Fapitec-SE/NEXSEN, by Fapemig (grant numbers PPM-00596-11, PPM-00306-09 and APQ-04124-10) and by INEO/CNPq Agencies from Brazil. Rodrigo F. Bianchi was also supported by CNPq (grant numbers 305646/2010-9 and PDE 200682/2011-3) and by Fapemig (grant numbers PPM-00596-11, PPM-00306-09 and APQ-04124-10).

Conflict of interest

None declare.

References

- Biggs P. Evidence for a significant timer error on a linear accelerator: consequences for a special therapy application. *Phys Med Biol* 1998;43:3139–43.
- William H. Patient safety and the medical physicist. *Med Phys Lett* 2011;38(6):I–II.
- Brennan TA, Leape LL, Laird NM, Hebert L, Localio AR, Lawthers AG, et al. Incident of adverse events and negligence in hospitalized-patients – results of the Harvard Medical-Practice study. *N Engl J Med* 1991;324(6):370–6.
- Hendee WR, Herman MG. Improving patient safety in radiation oncology. *Med Phys Lett* 2011;38(1):78–82.
- Bogdanich W. After stroke scans, patients face serious health risks. *N.Y. Times*; 2010.
- Bogdanich W. West Virginia hospital overirradiated brain scan patients, records show. *N.Y. Times*; 2011.
- Abdelaziz OS, Kandil A, El-Assall S, Rashed A. Linear accelerator-based stereotactic radiosurgery of intracranial meningiomas: results of the first 5 year of clinical practice. *Neurosurg Rev* 2011;34:87–9.
- Kingsley JW, Pearson AJ, Harris L, Weston SJ, Lidzey DG. Detecting 6 MV X-rays using an organic photovoltaic device. *Org Electron* 2009;10:1170–3.
- Kingsley JW, Weston SJ, Lidzey DG. Stability of X-rays detectors based on organic photovoltaic devices. *IEEE J Sel Top Quant Elec* 2010;16(6):1770–5.
- Graham SC, Fung S, Moratti SC, Friend RH. High sensitivity radiation sensing by photoinduced doping in PPV derivatives. *Synth Met* 1999;102(1):1169–70.
- Silva MDR, Gancalves AA, Silva RA, Marletta A. Gamma radiation effects on absorbance and emission properties of layer-by-layer PPV/DBS films. *J Non-Cryst Solid* 2010;356(44–49):2429–32.
- Borin JF, Brito ES, Nicolutti P, Graeff CFO, Bianchi RF. Low dose ionizing radiation detection using conjugated polymer. *Appl Phys Lett* 2005;86:131902-1–3-3.
- de Vasconcelos CKB, Bianchi RF. A blue-light dosimeter which indicates the dose accumulation by a multicoloured change of photodegraded polymer. *Sens Actuators B: Chem* 2009;143:30–4.
- Ferreira GR, de Vasconcelos CKB, Bianchi RF. Design and characterization of a novel indicator dosimeter for blue-light radiation. *Med Phys* 2009;36:642–4.

- [15] Ferreira GR, de Vasconcelos CKB, Silva MM, dos Santos FA, Pires JG, Duarte AS, et al. A novel and low-cost disposable device for phototherapy of neonatal jaundice. *Mater Res Soc Symp Proc* 2010;1, 1209-P03-03–1209-P03-09.
- [16] Ferreira GR, Nowacki B, deAvezedo ER, Akcelrud LC, Bianchi RF. Enhancing the photo-oxidation resistance of PPV-type polymers: effect of a radical scavenger addition. *Mater Res Soc Symp Proc* 2011;1(1286):1–5.
- [17] Ferreira GR, Nowacki B, deAvezedo ER, Magalhães A, Akcelrud LC, Bianchi RF. Controlling photo-oxidation processes of a polyfluorene derivative: the effect of additives and mechanism, in preparation.
- [18] Souza RV. Dose rate influence on deep dose deposition using a 6MV X-rays beam from a linear accelerator. *Braz J Phys* 2009;39(2):292–6.
- [19] International Atomic Energy Agency. Absorbed dose determination in external beam. Radiotherapy. Technical Reports Series No. 398, IAEA, Vienna; 2000.
- [20] Xiao-Dong L, Zheng X, Fu-Jun Z, Su-ling Z, Tian-Hui Z, Wei G, et al. Influence of small-molecule material on performance of polymer solar cells based on MEH-PPV:PCBM blend. *Chinese Phys B* 2010;19(11):118601.
- [21] Cumpston BH, Jensen KF. Photooxidative stability of substituted poly(phenylenevinylene) (PPV) and poly(phenylene acetylene) (PPA). *J Appl Polym Sci* 1998;69:2451–8.
- [22] Cumpston BH, Jensen KF. Photooxidation of polymers used in electroluminescent devices. *Synth Met* 1995;73(3):195–9.
- [23] Bianchi RF, Balogh DT, Tinani M, Faria RM, Irene EA. Ellipsometry study of the photo-oxidation of poly(2-methoxy-5-hexyloxy-*p*-phenylenevinylene). *J Polym Sci B* 2004;42:1033–41.
- [24] Schimitberger T, Ferreira GR, Saraiva MF, Bianchi AGC, Bianchi RF. X-ray dose detector based on color changing of light-emitting polymer-metal complex hybrid material. *Sens Act B: Chem B* 2012;168:131–7.