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Methodology for the radiation hardness assessment of organic semiconductors

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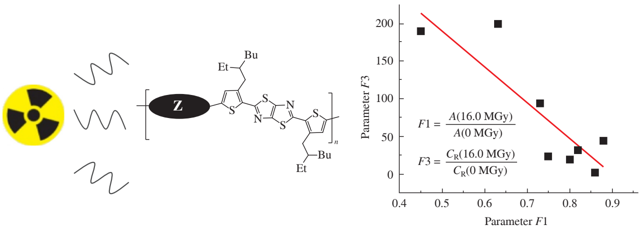
The first systematic study of the radiation hardness of a series of structurally similar conjugated polymers, model organic semiconductors, involves the set of numeric descriptors for quantitative benchmarking of their stability under exposure to the ionizing radiation. The conjugated polymers demonstrate surprisingly high radiation hardness and can tolerate huge doses of gamma rays up to 16 MGy much better than commodity types of plastic, which opens opportunities for their application in the development of radiation-tolerant organic electronics.



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Satellite telecommunication technologies are of paramount importance for modern society: this area is rapidly developing and is one of the fastest-growing markets.[1–6] Since humans are increasingly going beyond the planet Earth into outer space, special electronics with high radiation resistance are needed to ensure the reliability and safety of such missions.[7,8] In addition to space technologies, diagnostics and therapy of various diseases using ionizing radiation are actively developing.[9] X-ray systems are widely used to ensure the safety of important facilities, *e.g*., in airports, train stations, hospitals, government facilities.[10,11] The development of these technologies also requires components with high radiation resistance. Very recently, organic electronics has emerged as a promising technology that could be applied under harsh conditions due to its ability to tolerate ionizing radiation better than conventional crystalline silicon-based components.[12,13]

The development of this field is restricted by the lack of any reliable methodology to study the radiation hardness of organic semiconductors, and the relationships between the material structure and its tolerance to the ionizing radiation are completely missing. In this report, we make one of the first little steps to address the aforementioned issue by proposing a simple methodology for assessment of the radiation hardness of organic semiconductors.

We selected a model set of structurally similar polymers **P1**–**P9** reported before[14–16] (Figure 1) and explored their aging behavior under exposure to ^{60}Co gamma rays using the Gammatok-100 installation described previously.[17]

Using our accumulated background with the investigation of the UV light hardness of organic semiconductors,[18,19] we considered optical spectroscopy as a basic tool to assess the degradation dynamics of organic semiconductors in thin films. However, the immediate challenge was to find optically transparent substrate material that could tolerate high doses of ionizing radiation without the formation of so-called 'color centers' leading to the loss of transparency. For example, standard soda lime glass turns out brown or even black after receiving a relatively small dose of gamma rays (see Online Supplementary Materials, Figure S1, part *a*). Similar behavior was observed for many other optically transparent materials, *e.g.* CaF_2 turned deep blue after radiation exposure (Figure S1, part *b*). Organic polymer films appeared to be more stable but not enough for testing radiation hardness of organic semiconductors. Virtually all of them show spectral evolution in the UV and visible ranges upon exposure to gamma rays. We tested about ten different types of plastic foils, and they showed similar aging behavior as polyvinylidene difluoride (PVDF, Figure S1, part *c*) and polyethylene terephthalate (PET, part *d*). Some polymers (*e.g*., PET) demonstrated the development of photoluminescence (PL) in the visible range after exposure to gamma rays. The origin of this behavior is unclear, but it would complicate the assessment of the optical properties of the deposited organic semiconductor films after irradiation with gamma rays. Finally, most of the commodity plastic materials became extremely brittle after receiving the dose of 3–4 MGy, so the plastic films got destroyed to small dust-like particles by the radiation. Polyimide was the only suitable substrate material that could tolerate ultra-high doses of gamma rays up to 20 MGy (Figure S2) and probably even higher. However, polyimide has its intrinsic absorption at low wavelengths (<470 nm), which complicates the investigation of wide band gap organic semiconductors.

We prepared thin films of polymers **P1**–**P9** on polyimide plastic substrates, sealed them in air-tight bags inside argon- or nitrogen-filled glove box, and subjected them to different doses of gamma rays. After radiation exposure, the samples were introduced back to the glove box, and their optical spectra (UV-VIS absorption and PL) were measured. Thus, the entire

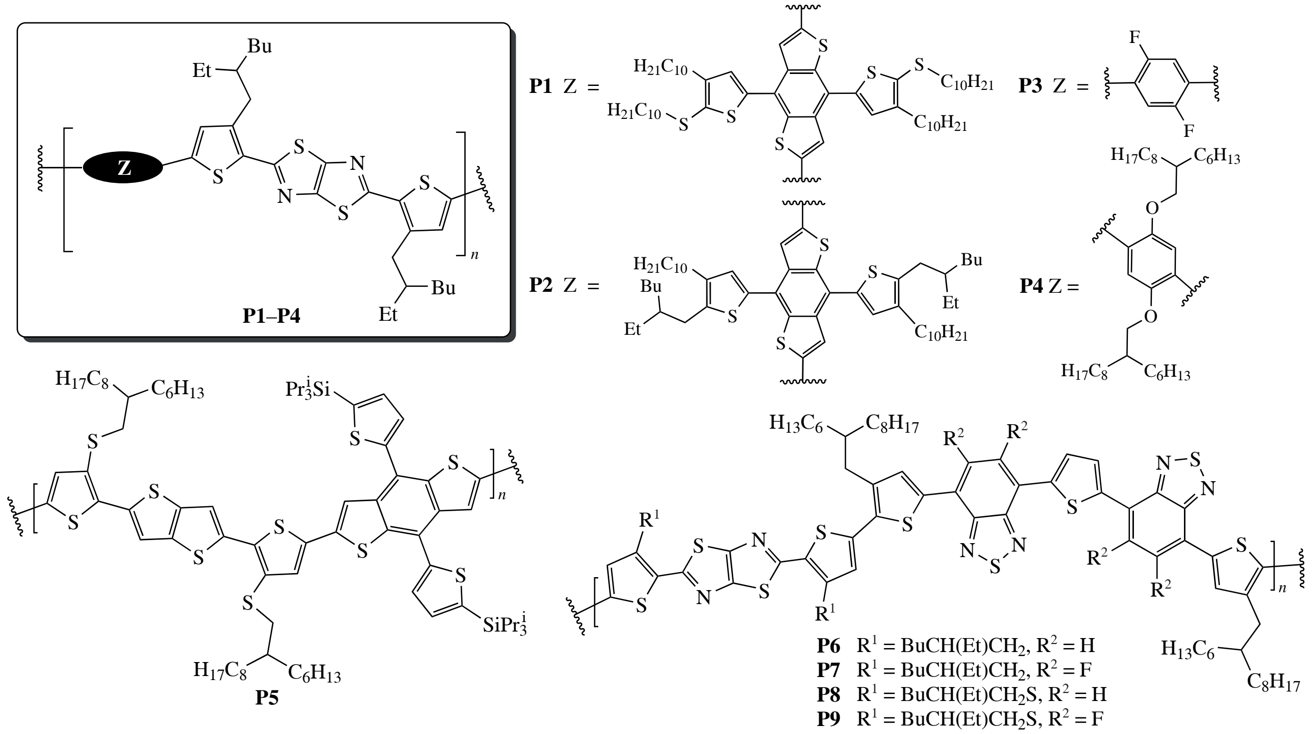


Figure 1 Molecular structures of the studied model polymers **P1**–**P9**.

experiment was performed under well-controlled anoxic conditions, so we could exclude the contribution of oxygen and moisture to the observed radiation-induced aging.

The exemplary spectral behavior is illustrated by polymers **P1** and **P2**. One could notice that both polymers demonstrate dose-dependent decay in the absorbance of their thin films [Figure 2(*a*)]. This kind of behavior is resembling the photobleaching of the polymer films under exposure to UV light[18,19] and has a very similar mechanism. Basically, the ionizing radiation generates reactive species within the thin films of organic semiconductor materials, which could be free radicals, singlet or triplet excitons, which could attack neighboring molecules, thus forming new bonds and leading essentially to cross-linking of the material. We have reported previously a facile cross-linking of conjugated polymers and small molecules under UV light exposure.[20] Similarly, organic semiconductors become completely cross-linked by gamma rays since their films become completely insoluble in organic solvents after receiving a dose of 100–500 kGy. Radiation-induced generation of defects promotes non-radiative quenching of excitons and photogenerated charge carriers, which is reflected in the rapid decay of the PL intensity upon exposure to gamma rays [Figure 2(*b*)].

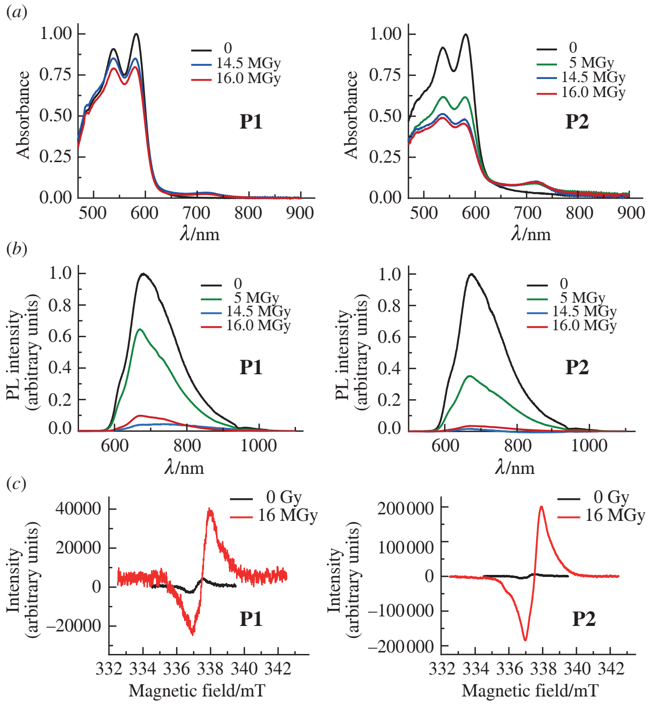


Figure 2 Effect of polymers **P1** and **P2** on the radiation-induced changes in the (*a*) UV-VIS, (*b*) PL and (*c*) ESR spectra.

Another important technique applied to monitor the radiation-induced degradation of conjugated polymers was electron spin resonance (ESR) spectroscopy, a sensitive tool to probe light-induced degradation of conjugated polymers and fullerene derivatives.[21] Owing to the high penetration ability of gamma rays, however, we could study directly powder samples sealed in the glass tubes with no need for thin film preparation, which was essential for the light-induced degradation experiments. However, since glass degrades faster than organic semiconductor materials, the measurements have to be performed in the non-exposed ESR tubes to obtain reliable results. Thus, we could observe a significant increase in the concentration of the radical species in the powder samples of conjugated polymers after they received the dose of 16 MGy: by a factor of 20 for **P1** and 190 for **P2** [Figure 2(*c*)].

It should be noted that **P2** showed roughly 10 times stronger accumulation of radical species than **P1**. Furthermore, faster PL quenching observed for **P2** correlates with more severe decay in the absorbance of this material after radiation exposure. Thus, a very minor modification of the chemical structure of the polymer by replacing two solubilizing alkyl groups in **P2** with alkylthio ones in **P1** results in the spectacular enhancement in the material radiation hardness. It is known that thiols and sulfides function as radioprotectors,[22] so alkylthio substituents in **P1** seem to have a very similar effect. However, the positioning of the alkylthio groups seems to be of essential importance. Thus, comparing polymers **P1**, **P2** with a very similar polymer **P5** suggests that the alkylthio substituents attached to the thiophene rings adjacent to the thiazolothiazole unit have no stabilizing effect. Therefore, polymer **P5** with alkylthio substituents in the ‘wrong position’ shows approximately the same aging dynamics as **P2** that has no thioalkyl groups (Figure S3).

Polymers **P3**, **P4** form another interesting group of materials. They differ from **P1**, **P2** by the structure of the Z-block (see Figure 1): benzodithiophene used in **P1**, **P2** is replaced with the substituted 1,4-phenylene units in **P3**, **P4**. This kind of modification clearly enhanced the radiation hardness of polymers since **P3**, **P4** demonstrate less pronounced spectral changes upon radiation exposure in comparison with **P1**, **P2** (Figure 3). It should be noted that exposure of the polymer films to gamma rays leads to the appearance of a low-energy absorption band with the maximum around 730 nm for **P1**–**P4**. Most likely, this absorption band manifests the formation of defects with the energy levels located within the gap of the pristine polymers **P1**–**P4**. This hypothesis is supported by the fact that these states are not emissive since we do not observe the appearance of any low-energy bands in the PL spectra while the emission is rapidly quenched. Furthermore, we did not observe any significant changes in the FTIR spectra of **P1**–**P4** powders upon exposure to 16.0 MGy of gamma rays (Figure S4), which allows us to exclude the formation of new chemical species with different optoelectronic properties. Thus, this absorption band is indeed defect-related, and its intensity is the weakest for polymer **P3**, which is followed by **P1** and then by **P2** and **P4**. By comparing the behavior of **P3** and **P4**, we could notice that **P1** shows more stable PL, while both polymers are comparable in terms of the accumulation of radical species [Figure 3(*b*),(*c*)]. Thus, even minor structural modification, like replacing ether groups in **P4** with fluorine atoms in **P3**, results in a spectacular enhancement in the radiation hardness of the material.

The last studies series of structurally similar polymers **P6**–**P9** demonstrated inconsistent behavior in the context of molecular structure–stability relationships. Polymer **P7** bearing fluorine substituents degraded notably less than the non-fluorinated analog **P6** after receiving a 16 MGy dose of gamma rays (Figure S5). However, for the pair of polymers **P8**, **P9**, the introduction of fluorine substituents had a clearly negative effect on the radiation hardness of the material. The presence of alkylthio substituents in **P8** could be responsible for its much higher stability as compared to polymer **P6** with the same backbone and alkyl substituents. However, for fluorinated polymers **P7** and **P9** the introduction of sulfur in the solubilizing side chains had no obvious effect on the radiation hardness of the materials. Interestingly, polymer **P8** showed the highest stability according to ESR spectroscopy data since the concentration of radicals in its powder practically did not change after exposure to a 16.0 MGy dose of gamma rays. On the contrary, polymer **P6** demonstrated a massive increase in the concentration of radical species by a factor of >3000. This value is at least 10 times higher than those for all other studied materials, so we could tentatively attribute this effect to the presence of some impurity rather than to the intrinsic behavior of the material.

Thus, we have investigated the radiation-induced aging of polymers **P1**–**P9** and provided some qualitative description of the observed effects based on the evolution of their spectral characteristics and possible correlations with their molecular structures. However, systematic investigation of different organic semiconductors and benchmarking their radiation hardness requires some qualitative descriptors for the materials’ stability. We propose to use three such descriptors, each based on one type of spectral data [Figure 4(*a*)]. First, we could compare semiconductor film absorbance before and after radiation exposure, which gives us parameter $F1$ [equation (1) in Figure 4]: the smaller its value, the less stable the material is. Similarly, parameter $F2$ [equation (2)] is based on the comparison of the PL intensity of the polymer thin films before and after exposure, so higher $F2$ values suggest reduced tendency for the formation of the radiation-induced defects and hence the higher material stability. Finally, parameter $F3$ [equation (3)] reflects the accumulation of radical species in the material after radiation exposure.

Table 1 gives the experimental values of the parameters $F1$–$F3$ determined for the studied materials. One could notice that parameter $F2$ does not correlate well with two other parameters. Most probably, this is due to very deep quenching of the PL of polymer films after receiving a huge dose of radiation (16 MGy): emission is almost absent for all the samples except **P5** and **P4**. Therefore, it may be recommended for future studies to determine $F2$ value for samples that received a smaller dose of gamma rays, *e.g.*, 1–5 MGy instead of 16 MGy.

Interestingly, parameters $F1$ and $F3$ show quite a decent correlation with each other if we exclude from consideration the

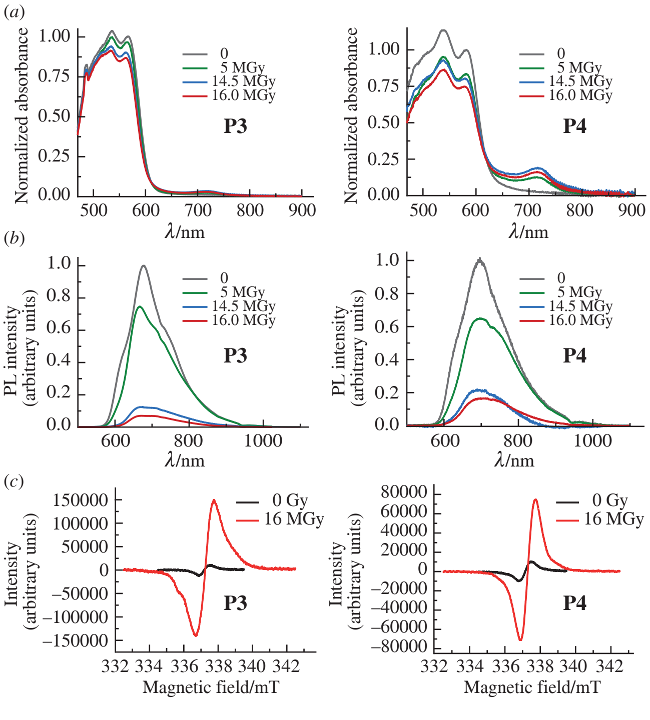
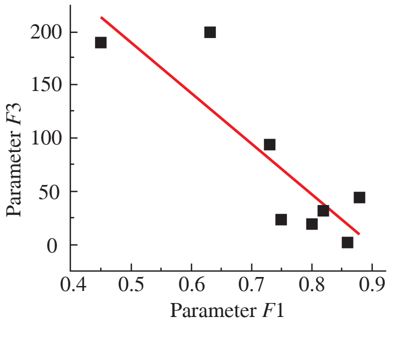


Figure 3 Evolution of (*a*) UV-VIS, (*b*) PL and (*c*) ESR spectra of polymers **P3** and **P4** upon exposure to different doses of gamma rays.

$$F1 = \frac{A(16.0\ \text{MGy})}{A(0\ \text{MGy})} \quad (1)$$

$$F2 = \frac{\text{PL}(16.0\ \text{MGy})}{\text{PL}(0\ \text{MGy})} \quad (2)$$

$$F3 = \frac{C_\text{R}(16.0\ \text{MGy})}{C_\text{R}(0\ \text{MGy})} \quad (3)$$



Equation	$y = a + bx$
Plot	E
Weight	No Weighting
Intercept	430.28013±84.1714
Slope	–479.87179±111.96
Residual Sum of Squa	10560.49269
Pearson's r	–0.86821
R-Square (COD)	0.75379
Adj. R-Square	0.71275

Figure 4 Equations used to calculate parameters $F1$–$F3$ and linear correlation between the values of $F1$ and $F3$.

Table 1 Parameters *F*1–*F*3: descriptors of the radiation hardness of polymers **P1**–**P9**.[a]

Polymer	Parameter *F*1	Parameter *F*2	Parameter *F*3
P1	0.80	0.10	20
P2	0.45	0.03	189
P3	0.88	0.07	45
P4	0.75	0.21	23
P5	0.63	0.53	200
P6	0.60	0.04	3399
P7	0.82	0.03	31
P8	0.86	0.03	1
P9	0.73	0.03	93

[a] All parameters calculated for thin films (*F*1–*F*2) or powders (*F*3) exposed to 16 MGy of gamma rays.

extremely high value suspiciously obtained for **P6**. The correlation could be fitted with a linear equation with the Pearson's correlation coefficient $r = 0.86$ (see Figure 4). This finding suggests that both *F*1 and *F*3 provide rather adequate benchmarking of the radiation hardness of polymers **P1–P9**.

To summarize, we have designed and presented here a possible research methodology for the systematic screening and assessment of the radiation hardness of organic semiconductors. The first relationships between the peculiarities of the molecular structures of the conjugated polymers **P1–P9** and their tolerance to the gamma rays exposure have been revealed. Numeric descriptors have been proposed for quantitative benchmarking of the radiation hardness of organic semiconductors. Very exciting was the observation that polymers **P1–P9**, being good representatives of organic semiconductors, have demonstrated higher radiation hardness than the vast majority of the commodity-type non-conjugated polymers, such as polypropylene, PET, PVDF, *etc*. This finding points to the bright future of organic semiconductors in the design of a new generation of electronics with supreme radiation hardness for application in harsh aerospace or terrestrial environments.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7820.

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