

## Supplementary file

### Wireless Chipless Printed Sensor Tag for Real-time Radiation Sterilization Monitoring

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## Raman and FTIR Analysis of irradiated PEDOT:PSS and PEDOT: PSS/PU films

The sensing mechanism of the printed sensor tags was investigated through Fourier transform infrared spectroscopy – attenuated total reflectance (FTIR-ATR) and Raman spectroscopy. The FTIR-ATR spectra of PEDOT:PSS, pristine PU, and 90wt% PU films at different radiation doses (0 kGy, 15kGy, and 30 kGy) are shown in **Fig. S1a**, **S1b**, and **S1c** respectively. **Fig. S1a** shows the FTIR-ATR spectra for PEDOT:PSS samples in the range from 1900 to 650  $\text{cm}^{-1}$  wavenumber. The characteristic vibration bands attributed to the C=C stretching and C-C stretching vibrations of the thiophene ring were identified at the 1524  $\text{cm}^{-1}$  and 1271  $\text{cm}^{-1}$  wavenumber, respectively.<sup>1, 2</sup> In addition, the stretching vibration bands ascribed to the C-S functional group were observed at the wavenumbers 946, 858, and 710  $\text{cm}^{-1}$ .<sup>3</sup> Similarly, the presence of the ethylenedioxy functional group was confirmed by the C-O-C stretching vibration peaks located at the wavenumbers 1161, 1120 and 1057  $\text{cm}^{-1}$ .<sup>4</sup> **Fig. S1a** shows a significant and gradual decrease in the peak intensity of the vibration bands associated with the C=C (1524  $\text{cm}^{-1}$ ), C-C (1271  $\text{cm}^{-1}$ ), C-S (946  $\text{cm}^{-1}$ ), and C-O-C (1120  $\text{cm}^{-1}$ ) functional groups of PEDOT polymer chains after radiation exposure. Similarly, **Fig. S1g** demonstrates a substantial decrease in the relative peak intensity of C-C, C-S, and C-O-C functional groups as compared to the C=C stretching vibration of PEDOT: PSS. This decrease in peak intensity reveals that exposure to high radiation dose changes the chemical structure of PEDOT polymer chains via chain scission. As a result, PEDOT polymer chains lost conductivity caused by a decrease in polymer chain length, particularly the polymer conjugation length, which is significantly important for charge transport in conductive polymers.

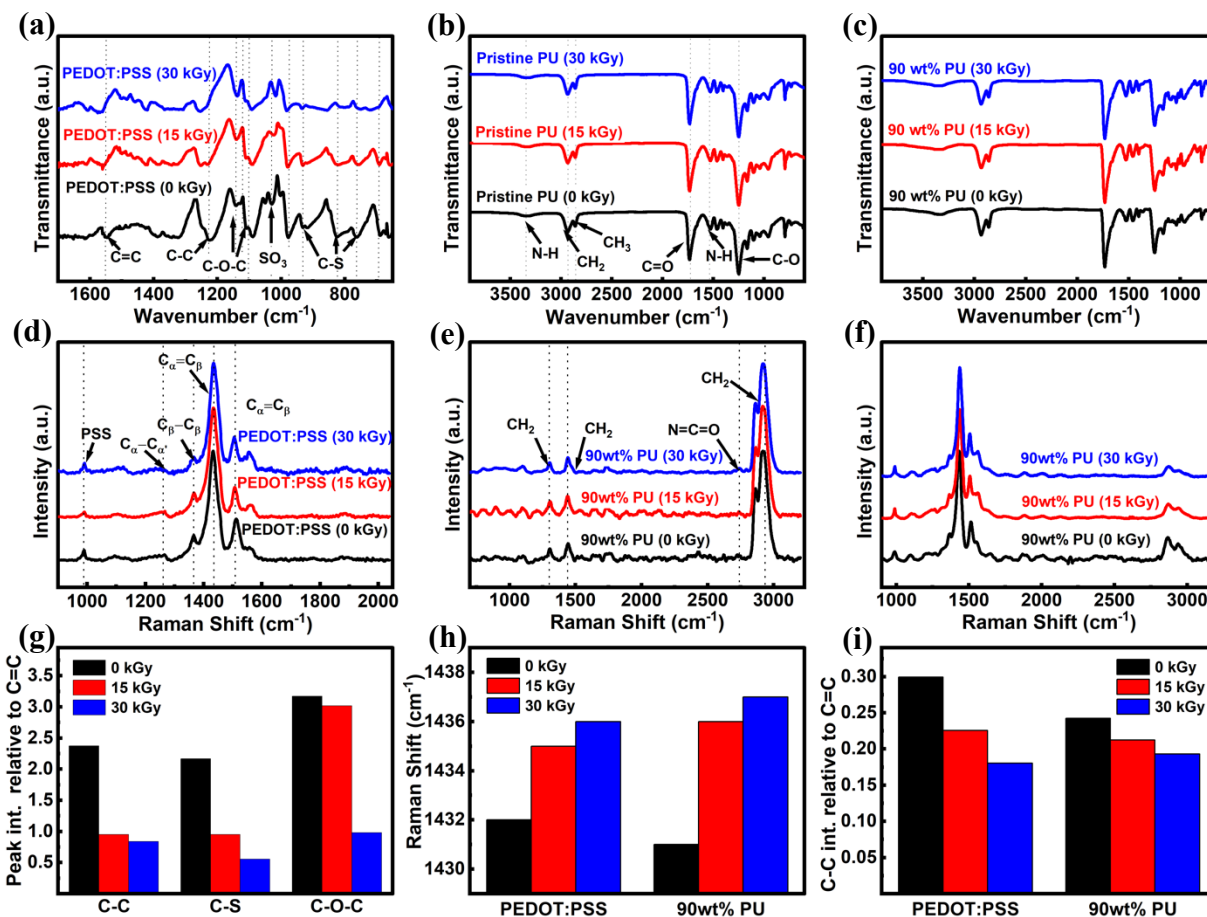
The effect of gamma radiation on pristine PU and 90wt% PU films was also studied. The FTIR-ATR spectra of PU and 90wt% PU films at different radiation doses are shown in **Fig. S1b** and **Fig. S1c**, respectively. The results show the identical FTIR-ATR spectra of pristine PU films collected at different radiation doses suggest a negligible change in the chemical structure of PU chains below 30 kGy. Inspection of **Fig. S1c** also indicates the dominance of the PU functional groups by completely overlapping with the vibrational band response of PEDOT:PSS functional groups.

To confirm the effects of gamma radiation on the PEDOT:PSS/PU blend, changes in their chemical structure were further evaluated by Raman spectroscopy under green excitation light (512 nm laser). The Raman spectra of PEDOT:PSS, pristine PU, and 90wt% PU films at different radiation doses (0 kGy, 15kGy, and 30 kGy) are shown in **Fig. S1d**, **S1e**, and **S1f** respectively. **Fig. S1d** displays the Raman spectra for PEDOT:PSS films in the range from 2050 to 650  $\text{cm}^{-1}$  wavenumber. The characteristic peaks at 1360  $\text{cm}^{-1}$ , 1436  $\text{cm}^{-1}$ , and 1500  $\text{cm}^{-1}$  were ascribed to the  $\text{C}_\alpha\text{-C}_\alpha$ , symmetrical  $\text{C}_\alpha\text{=C}_\beta$  and asymmetrical  $\text{C}_\alpha\text{=C}_\beta$  stretching vibrations of the thiophene ring in PEDOT polymer chains, respectively.<sup>5</sup> As shown in **Fig. S1d**, the peak intensity associated with the symmetrical  $\text{C}_\alpha\text{-C}_\alpha$  gradually decreased with radiation exposure. This decrease in peak intensity confirms the chain scission of the PEDOT polymer chains which is in good agreement with the previously discussed FTIR-ATR results and other reported studies.<sup>6</sup> In addition, a shift toward higher wavenumbers of symmetrical  $\text{C}_\alpha\text{=C}_\beta$  peak indicates a change in polymer chain conformation after radiation exposure.<sup>7</sup>

Finally, the effect of gamma radiation on pristine PU and 90wt% PU films was also investigated by Raman spectroscopy. The Raman spectra of PU and 90wt% PU films at different radiation doses are shown in **Fig. S1e** and **Fig. S1f**, respectively. As expected, the irradiated PU films exhibited a negligible change in the chemical structure of PU chains below 30 kGy. On the other hand, a gradual decrease in the peak intensity for symmetrical  $\text{C}_\alpha\text{-C}_\alpha$  confirms that chain scission of PEDOT:PSS is also present in 90wt% PU films.

Similarly, it was identified that gamma radiation induced a shift towards a higher wavenumber for the symmetrical  $C_{\alpha}-C_{\alpha}$  peak in 90wt% PU. Therefore, it is apparent that both, PEDOT:PSS and 90wt% PU films exhibited chain scission and polymer chain conformation changes (Fig. S1h and Fig. S1i).

In summary, these results suggest that PEDOT:PSS is responsible for the noticeable decrease in electrical conductivity of the sensing tags upon radiation exposure, while PU only functions as a polymer matrix to maximize the sensitivity to radiation exposure. The reason for the high radiation sensitivity of PEDOT:PSS/PU blend is explained by the thin electrical network formed by weakly connected PEDOT:PSS conductive regions within the blend structure. In the case of blend with 90wt% PU, the concentration of PEDOT:PSS lies in the percolation threshold transition. This means that any disturbance in the conductive network such as chain scission will lead to drastic changes in electrical conductivity upon radiation exposure. As a result, 90wt% PU blend exhibit higher radiation sensitivity than PEDOT:PSS films in the studied dose range.



**Figure S1.** Vibrational spectroscopy of PEDOT:PSS/PU blend; FTIR-ATR spectra of (a) Pristine PEDOT:PSS, (b) Pristine PU, and (c) 90wt% PU blend; Raman spectra of (d) Pristine PEDOT:PSS, (e) Pristine PU and (f) 90wt% PU; (g) Peak relative intensity change of C-C, C-S and C-O-C bonds to C=C bonds in PEDOT:PSS after radiation exposure; (h) Comparison of C-C relative intensity change after radiation exposure in PEDOT:PSS and 90wt% PU blend and (i) Raman shift of C=C asymmetrical vibrations in PEDOT:PSS and 90wt% PU blend after radiation exposure.

## References

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