Probing the high radiation tolerance of minor actinide selective zirconium phosphonate sorbents

Supporting information

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Thermogravimetric analysis (TGA)

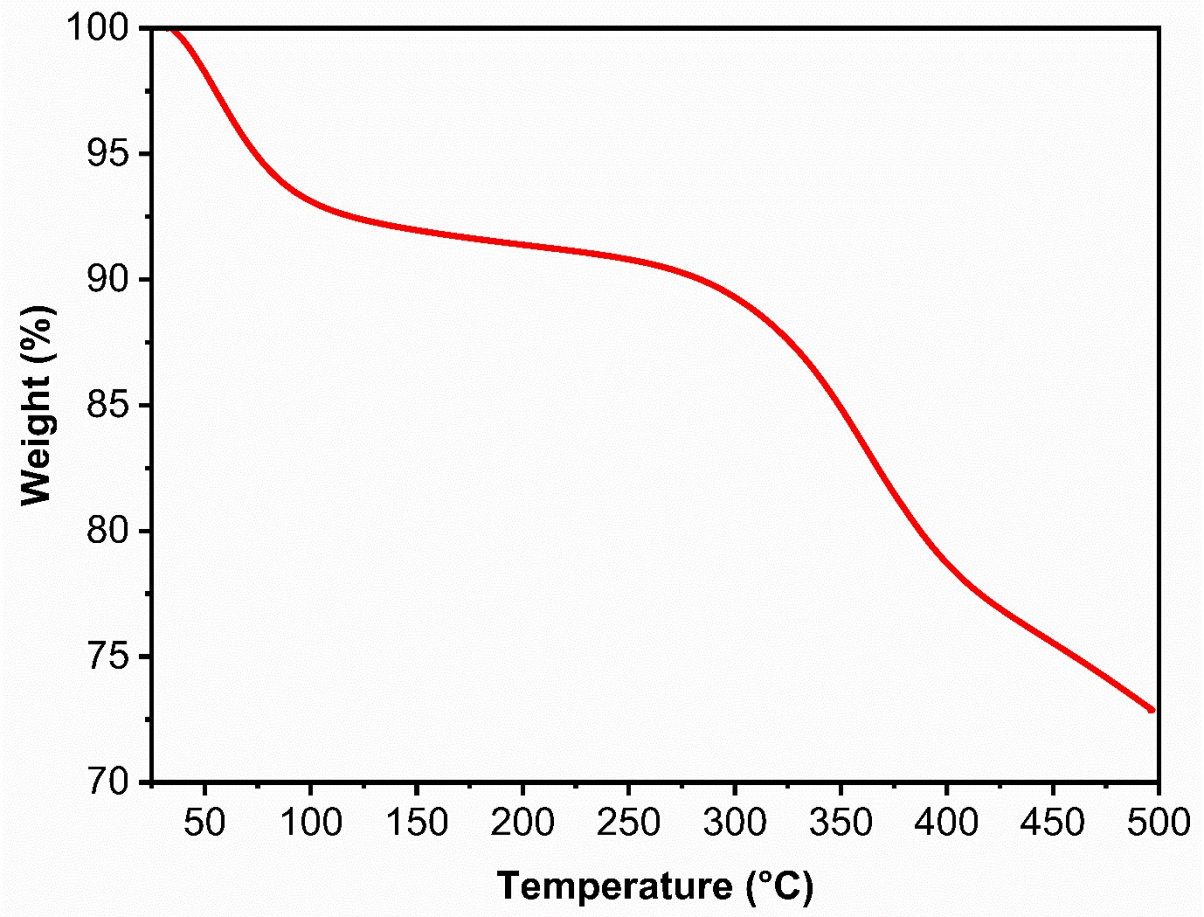

Figure S1. *TGA of ZrPTP under N_2 gas flow.*

To prevent misinterpretation of the gas measurement results due to the radiolysis of water, it was necessary for residual water to be removed prior to irradiation. Hence, thermal treatment of the sample was performed. Previous work has demonstrated that the sorption capacity of ZrPs can be damaged by thermal treatment at temperatures nearing 100 °C.[1] This is thought to be due to collapsing of the pores within the sorbent as water is removed, thereby reducing the surface area for sorption. Thus, TGA was used to determine the lowest temperature at which absorbed H_2O could be removed whilst still preserving sorption capacity. Figure S1 depicts the TGA results for ZrPTP. As shown, an approximate 10% change in weight can be observed initially between 30 °C and 275 °C. This was assigned as the removal of adsorbed H_2O from ZrPTP. Beyond 275 °C, a further approximate 17% change in weight is seen, which was assigned to the onset of thermal degradation of the PTP ligand. Given 100 °C is known to damage the sorption capacity of ZrPs, it was necessary to select a significantly lower temperature for thermal treatment. Based on the TGA results (Figure S1), 50 °C was selected as an appropriate compromise for thermal treatment given that removal of H_2O is possible at this temperature. This was supplemented with continuous vacuum during thermal treatment, as vacuum was reported to have minimal impact on the sorption capacity of ZrPs.[1]

Scanning electron microscopy (SEM)

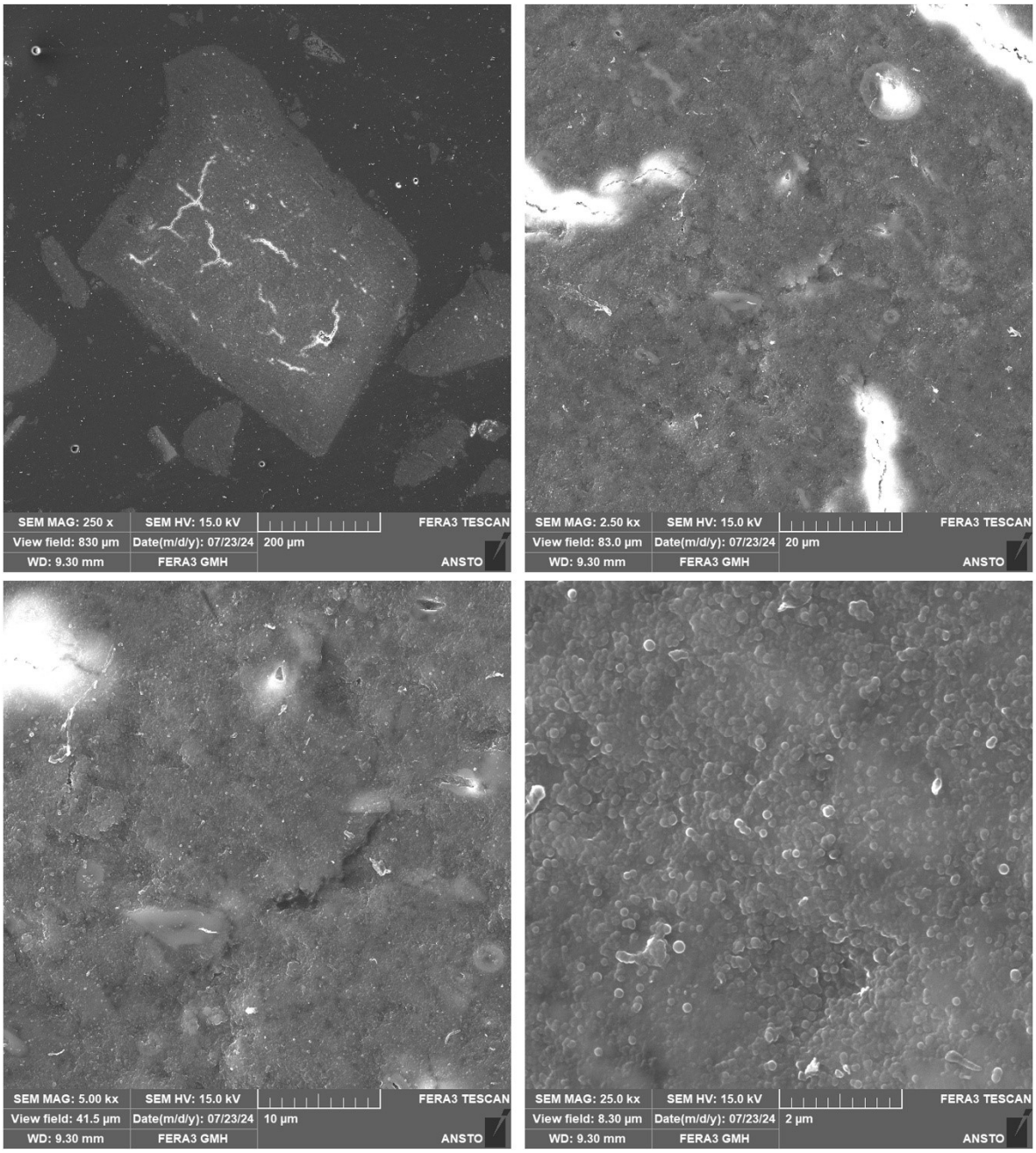

Figure S2. *SEM images of ZrPTP at 250, 2.5k, 5k and 25k magnification.*

Zr K-edge Extended X-ray Absorption Fine Structure (EXAFS)

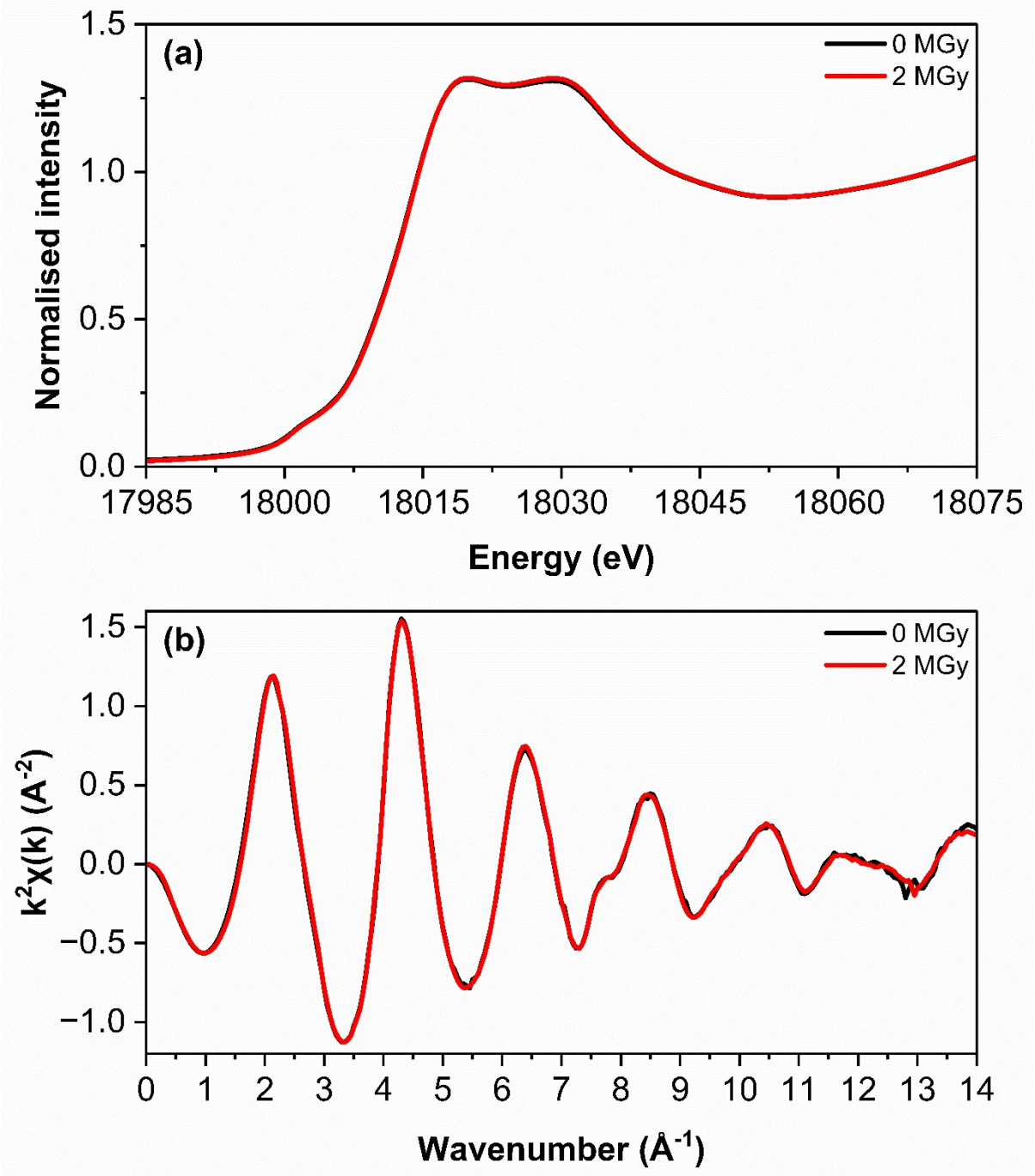

Figure S3. *Zr K-edge measurements of ZrPTP at irradiation doses of 0 and 2 MGy shown as the (a) XANES and (b) k2-weighted EXAFS.*

Atomic Pair Distribution Function (PDF)

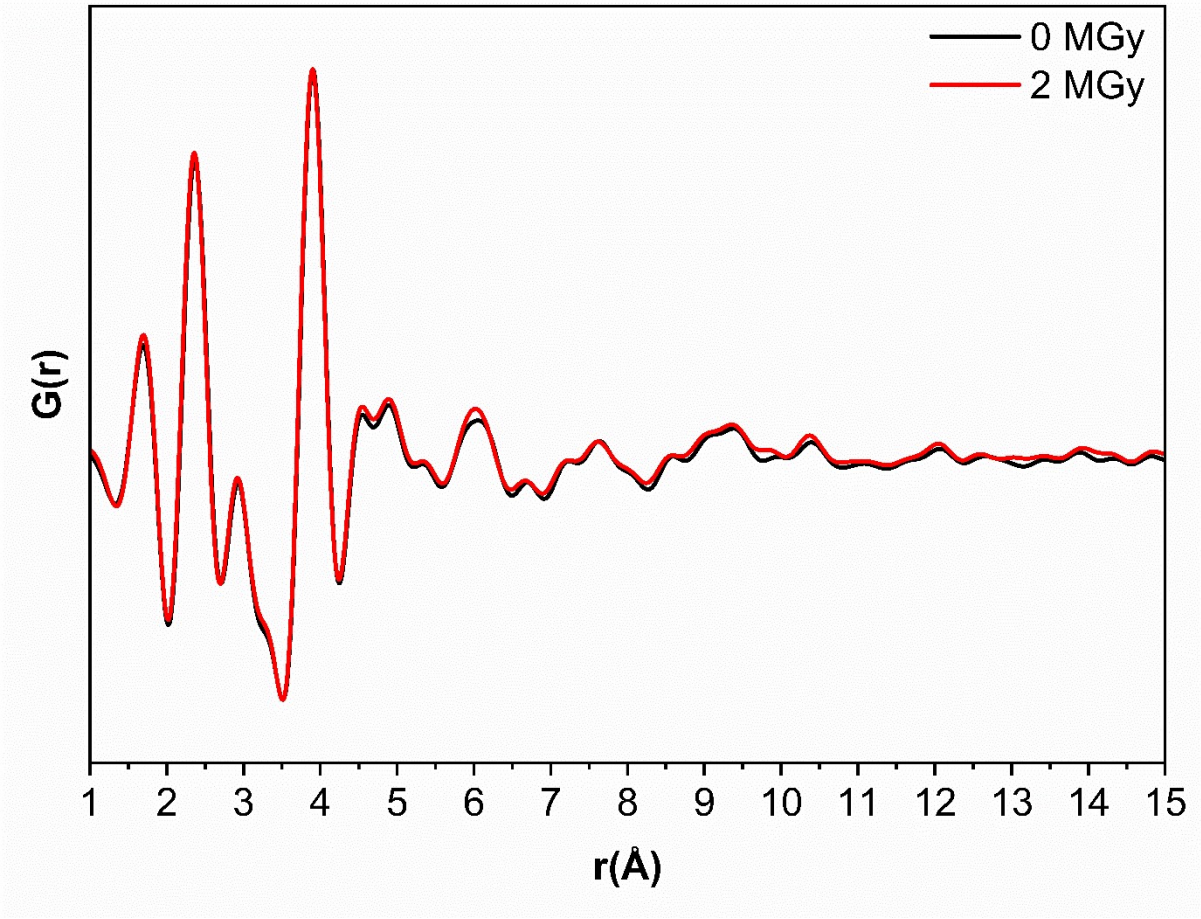

Figure S4. *Atomic PDF of ZrPTP at irradiation doses of 0 and 2 MGy.*

Fourier Transform Infrared Spectroscopy (FTIR)

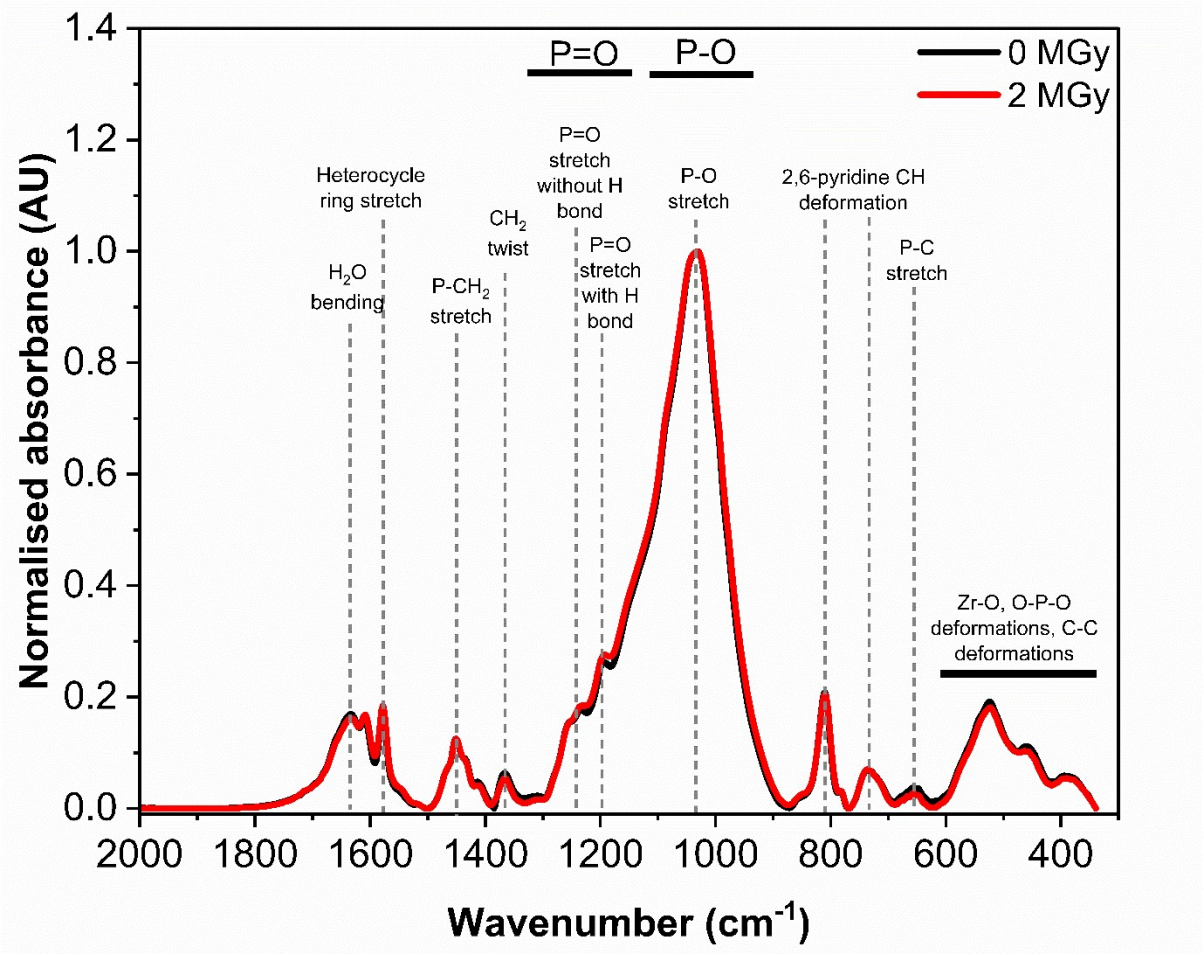

Figure S5. *FTIR spectra of ZrPTP at irradiation doses of 0 and 2 MGy.*

The FTIR spectra of ZrPTP is identical before and after irradiation, as shown in Figure S4, suggesting that the material is unaffected by irradiation. FTIR bands assignments have been assigned according to literature. Bands from 1800 to 600 wavenumber (cm^{-1}) have been assigned based on previous assignments by Veliscek-Carolan and Rawal[2], and Socrates[3]. The 600 to 340 wavenumber (cm^{-1}) region identities are difficult to determine and thus are broadly assigned; Zirconia, C-C deformations and O-P-O deformations are all known to show absorbance bands in this region.[3-7]

C K-edge Near Edge X-ray Absorption Fine Structure (NEXAFS)

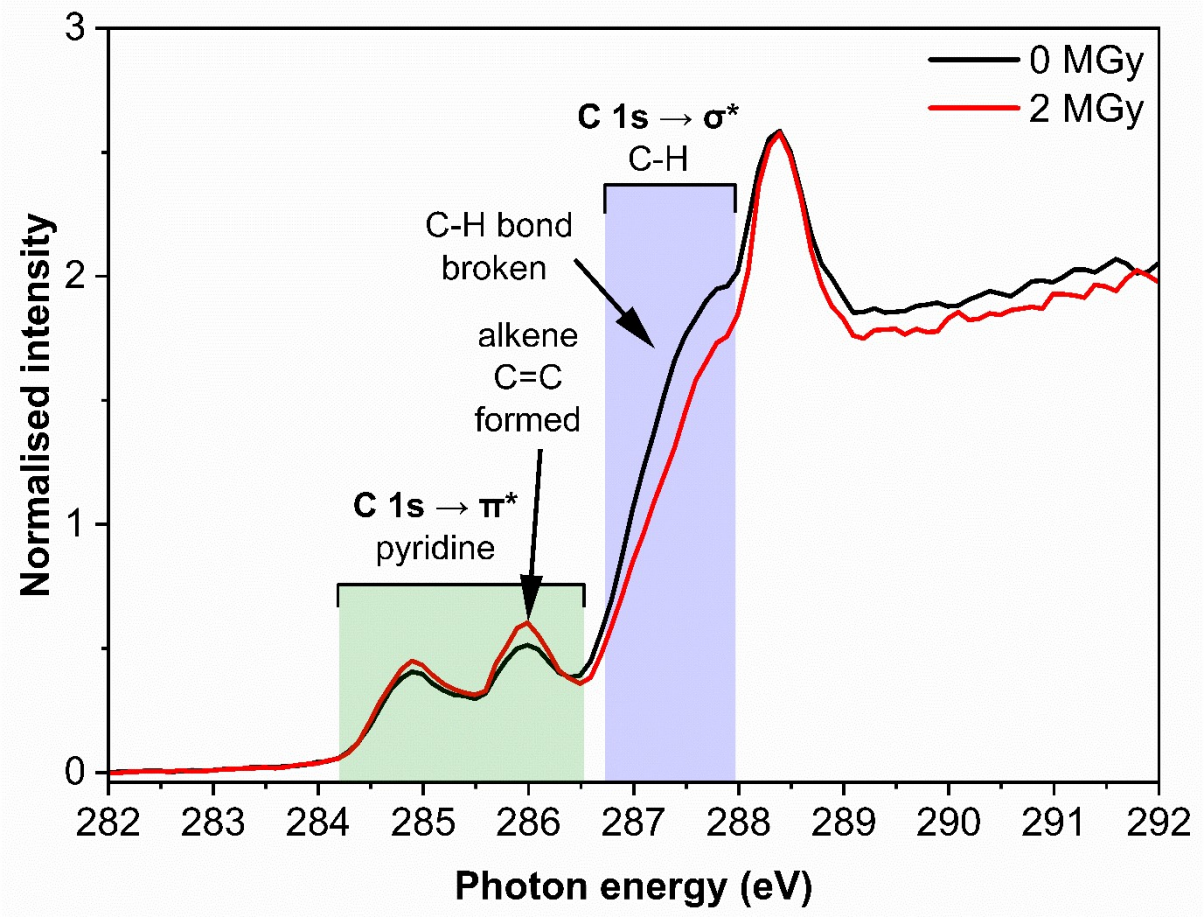

Figure S6. *C K-edge NEXAFS of ZrPTP at irradiation doses of 0 and 2 MGy.*

Figure S6 depicts the C K-edge NEXAFS of ZrPTP at radiation doses of 0 and 2 MGy. The peaks at 284.9 and 286 eV are characteristic of the pyridine C 1s to π* transitions, split by chemical shift as a result of distance to the N atom.[8,9] The broad peak (labelled B) has been assigned to the aliphatic chain C-H bonds as 1s to σ*.[8,10] The peak at 288.4 eV, which appears unchanged, may be largely contribution from the background and substrate.

References

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