Electronic supplementary materials *Mendeleev Commun.*, 2025, **35**, 688–691

Methodology for the radiation hardness assessment of organic semiconductors

Petr M. Kuznetsov, Tatiana N. Khokhlova, Galina A. Kichigina, Pavel P. Kushch, Dmitry P. Kirukhin and Pavel A. Troshin

Contents

1. Experimental

1.1 Sample preparation

All polymer solutions (8-10 mg/ml) were prepared inside the nitrogen-filled glove box using anhydrous chlorobenzene or1,2-dichlorobenzene as solvents (Sigma-Aldrich). Polyiimide plastic slides (25*25 mm) were used as substrates for deposition of the polymer films. Polyimide substrates were attached to the glass at the stage of spin-coating to maintain the sample planarity. The spin-coating rate was adjusted to obtain approximately the same film absorbance of 0.5-0.6 at the maximum of the major absorption band at long wavelengths. Powder samples of polymers (10-30 mg) were placed in the clean glass tubes and sealed in inert atmosphere without any exposure to air. After radiation exposure, the sample tubes were opened inside the glove box and materials were transferred to ESR tubes for the measurements. Afterwar the ESR measurements, the closed sample tubes were introduced back to the glove box to avoid aby contact with air.

1.2 Gamma rays exposure

The studied thin film deposited on PI substrates were placed in metal containers and sealed in 4-5 layers of Al-laminated plastic foil, which is typically used to form cases of pouch-type lithium-ion batteries. All these preparations were performed inside MBraun glove box with O_2 and H_2O content below 0.1 ppm. Afterwards, the package with the samples or sealed glass tubes were taken outside glove box and exposed to the ^{60}Co source of gamma rays with the dose rate of 2 Gy/s using the Gammatok-100 setup. The temperature inside the irradiation chamber was 45±2 ^{o}C. The dose rate calibration in the setup is carried out using the ferrosulfate method and the measurement error does not exceed 10%. After the samples received the first dose of gamma rays (e.g. 5 MGy), they were transferred back inside the glove box, the package was opened, the samples were characterized by spectroscopy inside the same glove box and then packed again for the next gamma rays exposure cycle. Thus, the final dose of 16 MGy was accumulated for the same samples in several iterations.

1.3. Characterization of the samples

The UV-Vis absorption spectra were measured using an AvaSpec-2048-2 UV-vis fiber spectrometer integrated into the MBraun glove box. FTIR spectra were measured inside the glove box using Perkin Elmer Spectrum Two spectrometer in Attenuated Total Reflection (ATR) mode using KRS5/diamond prism. Steady-state PL spectra were measured under a nitrogen atmosphere inside a glove box using Ocean Insight QE Pro spectrometer and a 450 nm laser as the excitation source. ESR spectra were measured using benchtop ADANI CMS8400 spectrometer. The center field was 3380 G, sweep width 50 G, the modulation amplitude was 1250 mG, power attenuation 15 dB.

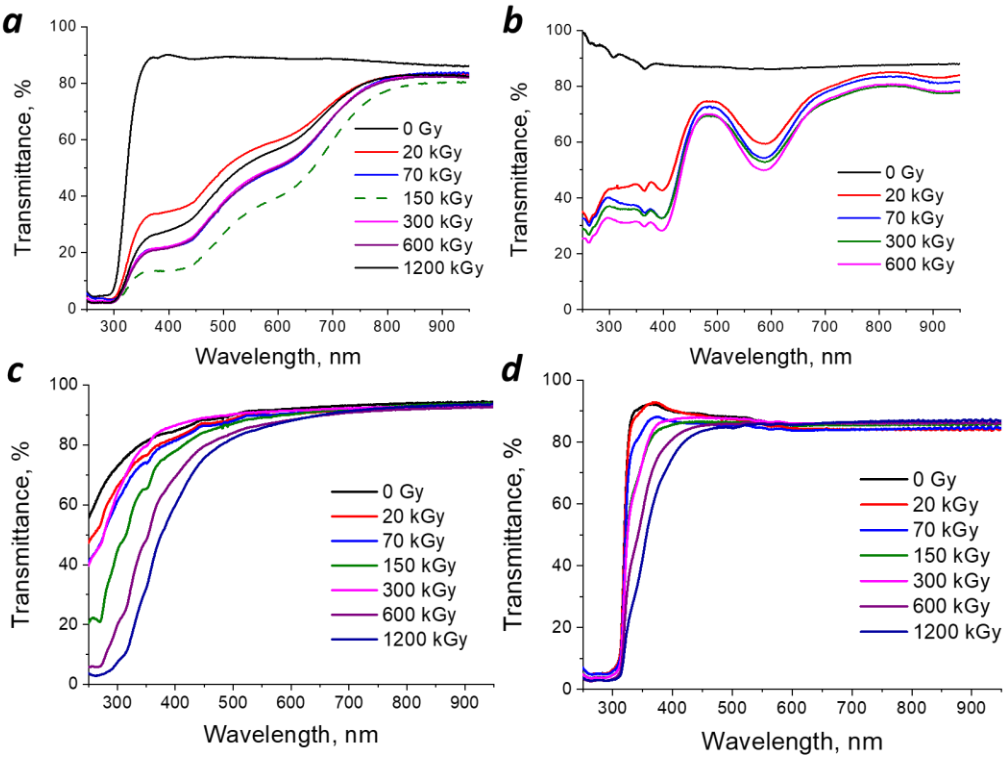

Figure S1. The evolution of the optical spectra of the standard soda lime glass (a), CaF_2 slides (b), PVDF film (c) and PET film (d) upon exposure to gamma rays.

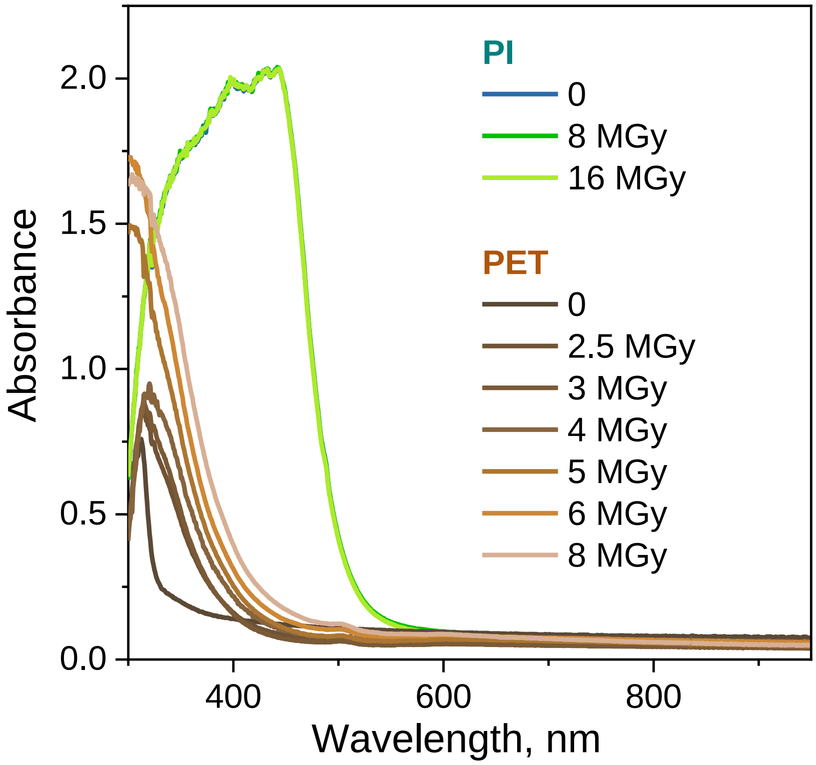

Figure S2. Comparing the radiation-induced changes in the absorption spectra of PET and polyimide plastic film substrates

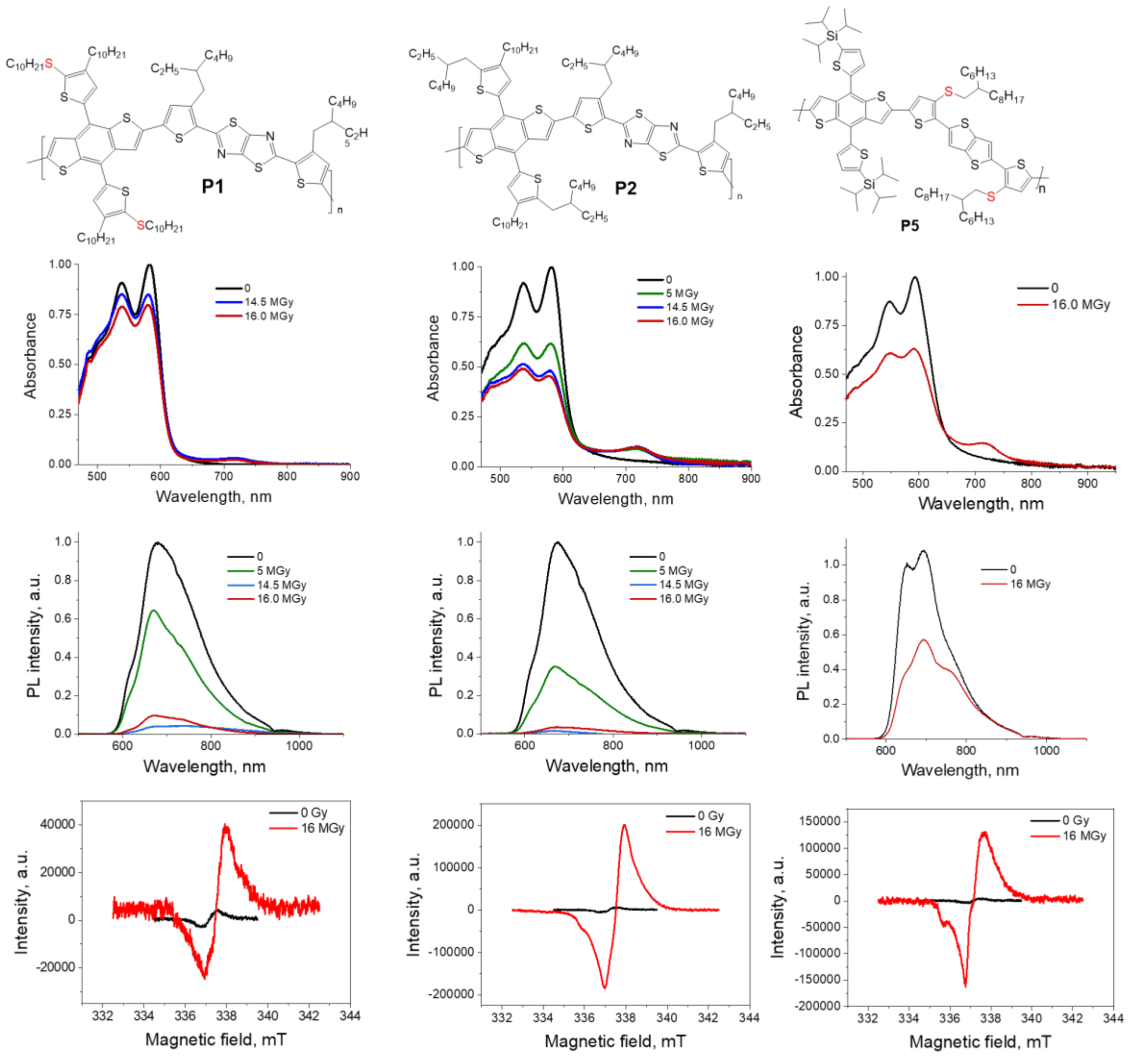

*Figure S3. Molecular structures of **P1**, **P2** and **P5** (a) and the evolution of their UV-vis (b), PL (c) and ESR (d) spectra upon exposure to different doses of gamma rays.*

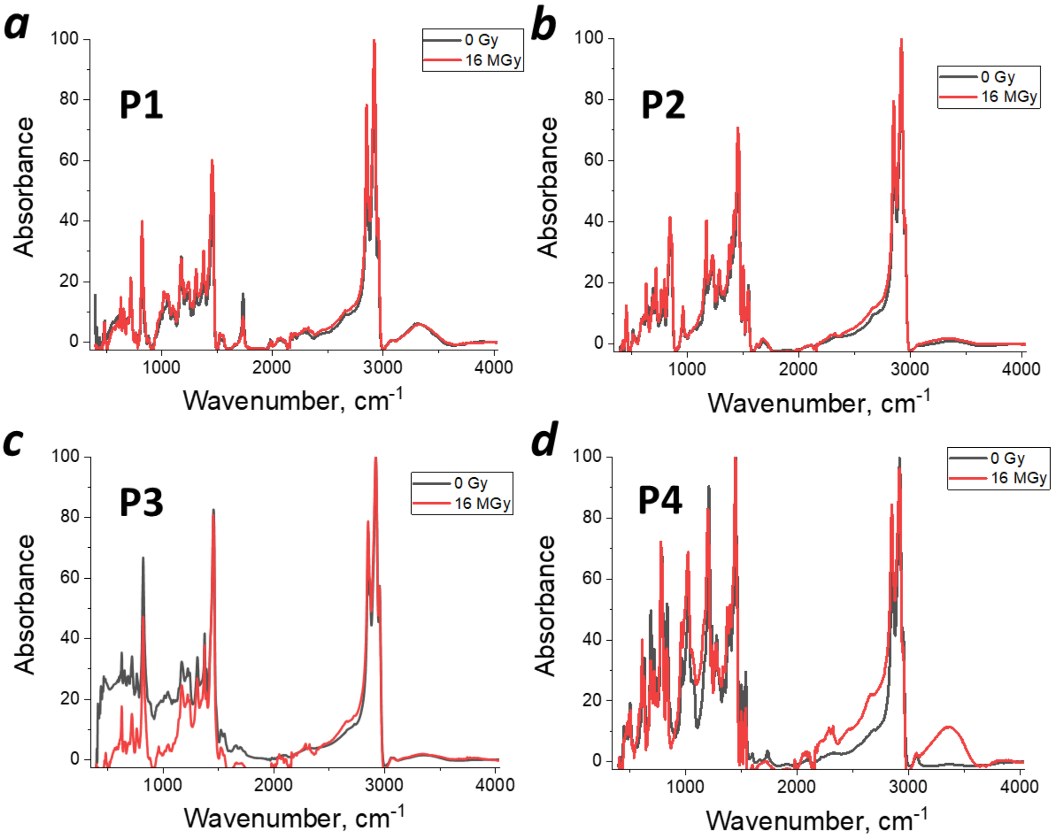

Figure S4. Comparison of the FTIR spectra of polymers ***P1*** *(a),* ***P2*** *(b),* ***P3*** *(c) and* ***P4*** *(d) before and after exposure to the 16 MGy dose of gamma rays.*

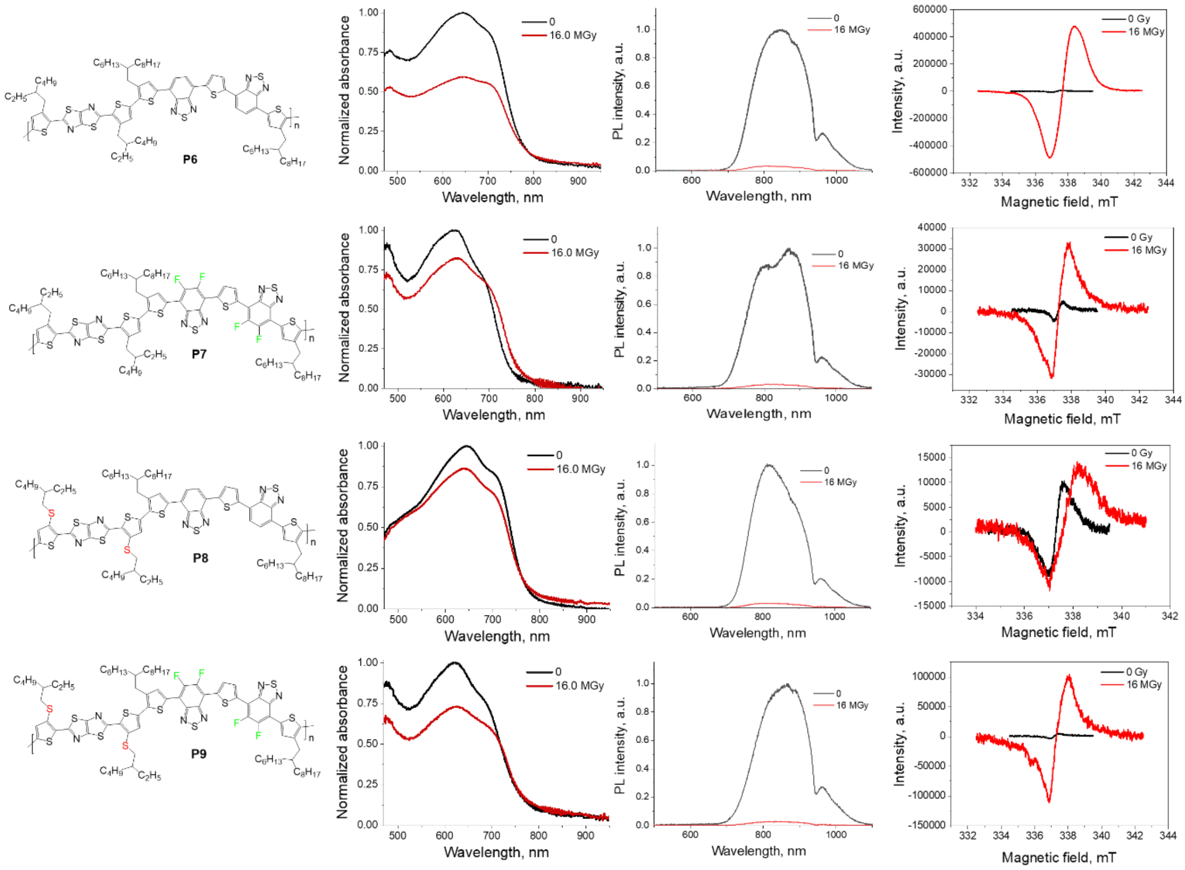

Figure S5. From left to right: molecular structures of ***P6-P9****, the evolution of their UV-vis, PL and ESR spectra upon exposure to 16 MGy dose of gamma rays.*