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ARTICLE TYPE

X-ray induced ultrafast charge transfer in thiophene-based conjugated polymers controlled by core-hole clock spectroscopy[†]. Electronic Supplementary Information.

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1 APPENDIX A: SAMPLES CHARACTERISATION

Depending on the procedure used for a P3HT film preparation, two orientations of the polymer chains on the substrate are possible[1]. In the edge-on orientation, the self-organised lamella sheets are positioned perpendicular to the substrate, while in the face-on orientation, the lamellae are fixed parallel to the substrate.

Following the prescriptions provided in literature[2], we have chosen the rotational spin-coating frequency of 2000 revolutions per minute and the chloroform solution concentration of 5 mg/ml that lead to formation of a film with face-on orientation. Furthermore, our x-ray diffraction analysis of the film, using a Cu Kα source in a symmetric $\theta/2\theta$ geometry, revealed a signature at $24°$ corresponding to the inter-chain $\pi - \pi$ stacking, which indicates a face-on orientation of the film[3,4]. In addition, no sharp structures typical for an edge-on orientation were observed. The $\sim$34 nm thickness of the P3HT film was determined using atomic force microscopy.

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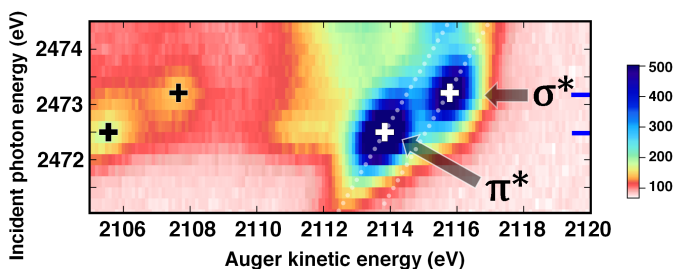

Fig. S1 2D maps of S KL$_{2,3}$L$_{2,3}$ Auger spectra recorded in P3HT film at grazing incidence. Transitions to the $2p^{-2}(^1S)\pi^*$ and $2p^{-2}(^1S)\sigma^*$ final states are indicated with black crosses. Transitions to the $2p^{-2}(^1D)\pi^*$ and $2p^{-2}(^1D)\sigma^*$ states, indicated with white crosses, are labelled as π^* and σ^*. Blue lines indicate the corresponding resonant photon energies. Diagonal dotted lines show dispersive behaviour of resonant structures. The map is normalised to the background. The colour-coded intensities are on a logarithmic scale.

The measurements presented in Fig. 3 of the main text were performed at normal incidence with the polarisation of the incident x-ray beam parallel to the sample surface. Assuming a face-on orientation of the P3HT film, in this geometry one can expect a dominant excitation of the S $1s^{-1}\sigma^*$ state. Indeed, this can be observed in Fig. 3 of the main text. For comparison, Fig. S1 shows a 2D map of S KL$_{2,3}$L$_{2,3}$ Auger spectra for P3HT measured in grazing incidence geometry, where the x-ray beam polarisation is perpendicular to the sample surface, leading to a primary excitation of the S $1s^{-1}\pi^*$ state. Note, that a dominant excitation of the S $1s^{-1}\pi^*$ state in the case of grazing incidence geometry and a resulting overlap of the strong resonant $2p^{-2}\pi^*$ feature with a weak low-energy peak, prevents us from a reliable fitting analysis in the whole photon energy range of the 2D map and therefore, does not allow revealing a possible CT process in this geometry.

A strong angular dependence observed for the P3HT sample, demonstrating dominant excitation of the S $1s^{-1}\sigma^*$ state for normal incidence, and the S $1s^{-1}\pi^*$ state for grazing incidence geometry, further corroborates the face-on orientation of the P3HT conjugate plane.

Note that our measurements did not reveal angular depen-

dence for the PT powder sample, which is consistent with the isotropic morphology of the powdered polymer. Similarly, measurements (not shown here) of a PT film, prepared using a potentiostatic electrochemical deposition technique, lack angular dependence. This points at a poor organisation of the PT film structure, probably related to the imperfect deposition conditions. Therefore, these measurements were excluded from the data analysis.

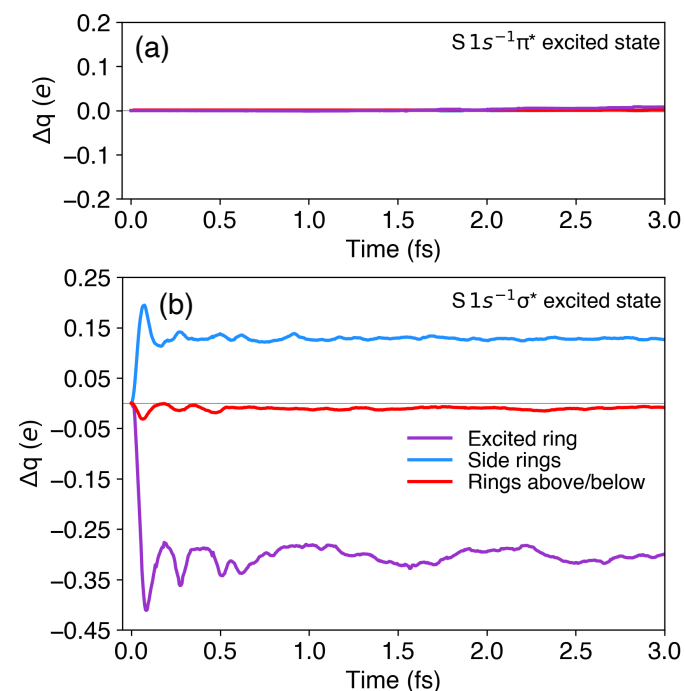## 2 APPENDIX B: EHRENFEST MOLECULAR DYNAMICS IN P3HT FILM

Fig. S2 Bader charge analysis in P3HT using EMD formalism for the first 3 fs of simulation considering only the excited thiophene ring and its nearest neighbours for (a) $S\,1s^{-1}\pi^*$ and (b) $S\,1s^{-1}\sigma^*$ states. The gray line denotes $\Delta q = 0$. Negative (positive) values indicate electron depletion (accumulation).

RT-TDDFT simulations can be compared to the Ehrenfest molecular dynamics (EMD) formalism[5,6]. In this case, the electronic wavefunction evolution is coupled to the nuclei motion in a mean-field approach, obtained by averaging over all quantum mechanical states. Bader charge analysis performed for P3HT using EMD for the first 3 fs of propagation (see Fig. S2), shows very similar results to RT-TDDFT simulations presented in Fig. 9 of the main text. Therefore, the choice of neglecting the nuclear motion in the RT-TDDFT approach does not seem to affect the CT process taking place within the first fs after these specific core-excitations.

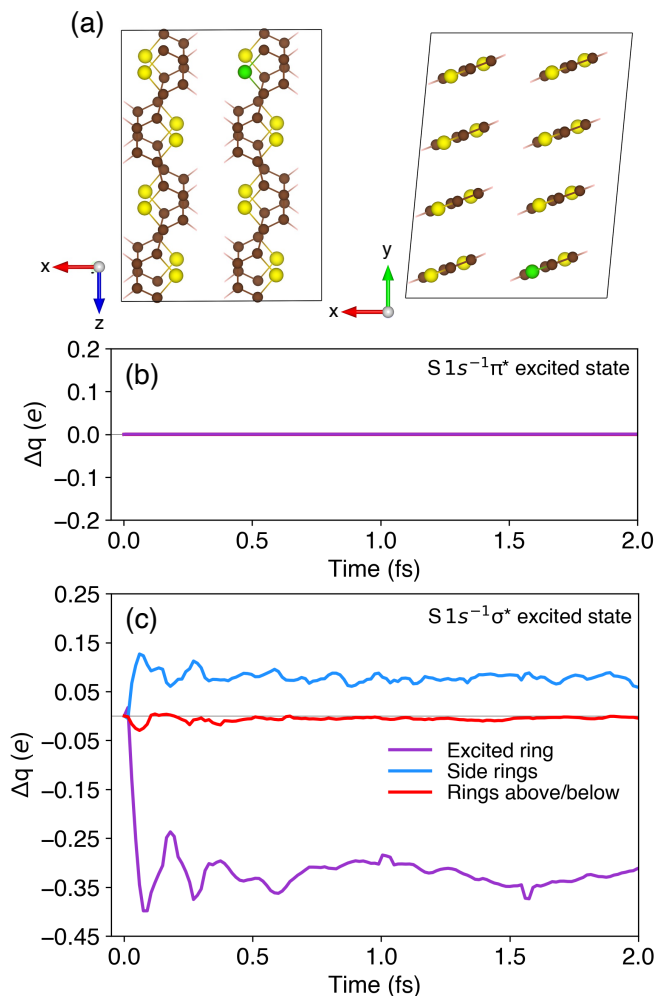## 3 APPENDIX C: RT-TDDFT SIMULATIONS IN PT FILM

Fig. S3 (a) Ball and stick representation of PT simulation cell employed in the RT-TDDFT simulations. colour code: brown for carbon, yellow for sulfur, green for chlorine (Z+1 approximation), light pink for hydrogen. (b) and (c) Bader charge analysis in $S\,1s^{-1}\pi^*$ and $S\,1s^{-1}\sigma^*$ core-excited states for the first 2 fs of simulation considering the excited thiophene ring and its nearest neighbours. The gray line denotes $\Delta q = 0$. Negative (positive) values indicate electron depletion (accumulation).

Notes and references

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