Supplementary Information: Ultrafast magnetisation dynamics in a chromium-based Prussian blue analogue

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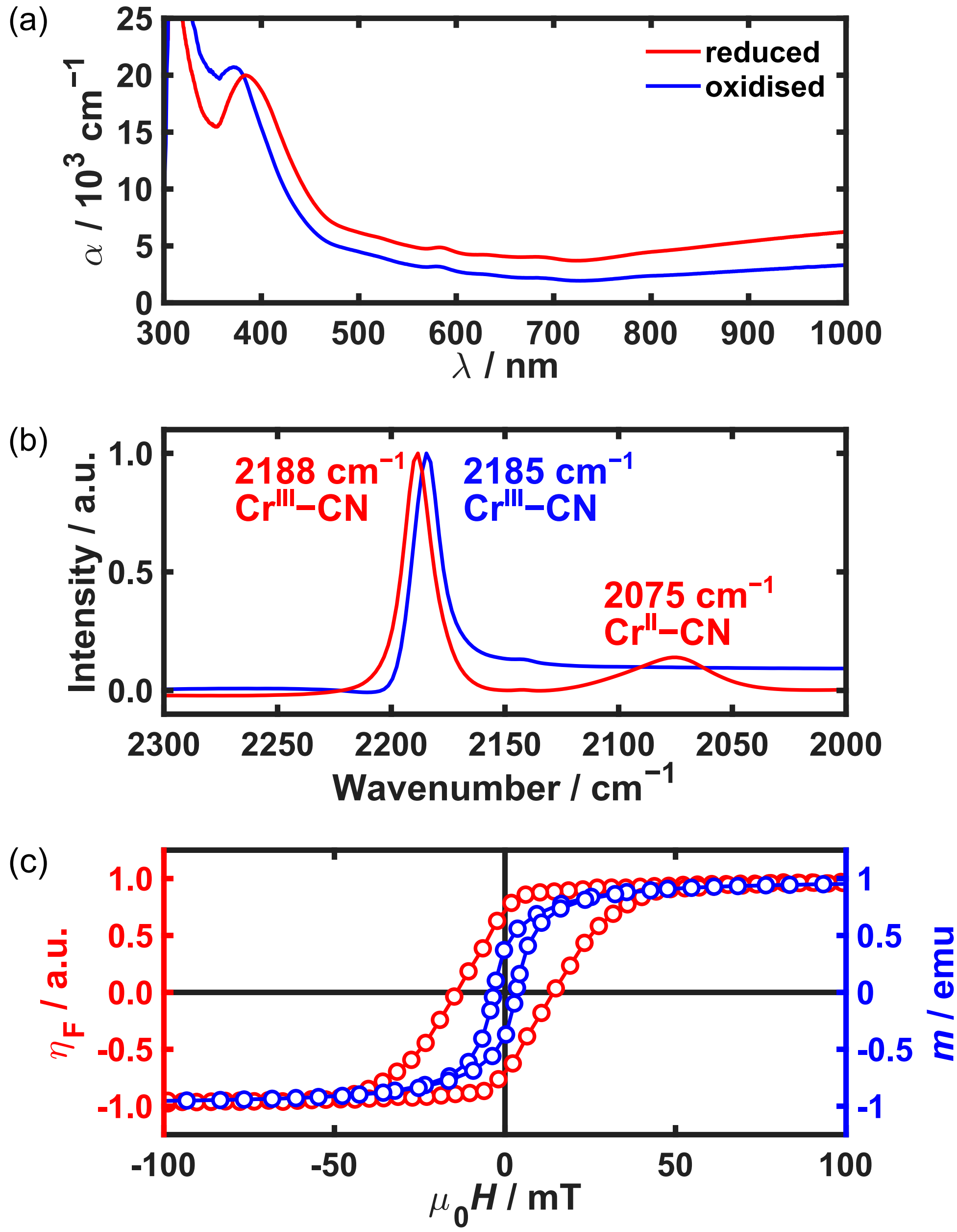

Fig. S1 Characterisation of Cr−Cr Prussian blue analogue (PBA) films before and after significant air exposure. (a) UV-visible-NIR transmittance spectra recorded for a single exposed film upon synthesis and after air exposure. (b) Fourier-transform IR (FT-IR) reflectance spectra recorded for a freshly made film *vs.* another film subject to air exposure. (c) Magnetic hysteresis loops recorded for reduced and oxidised films at 80 K. Data for the reduced film were obtained through Faraday ellipticity measurements using a 400 nm beam originating from the optical parametric amplifier at a repetition rate of 20 kHz (red, left axis), while data for the oxidised film were obtained through SQUID magnetometry (blue, right axis).

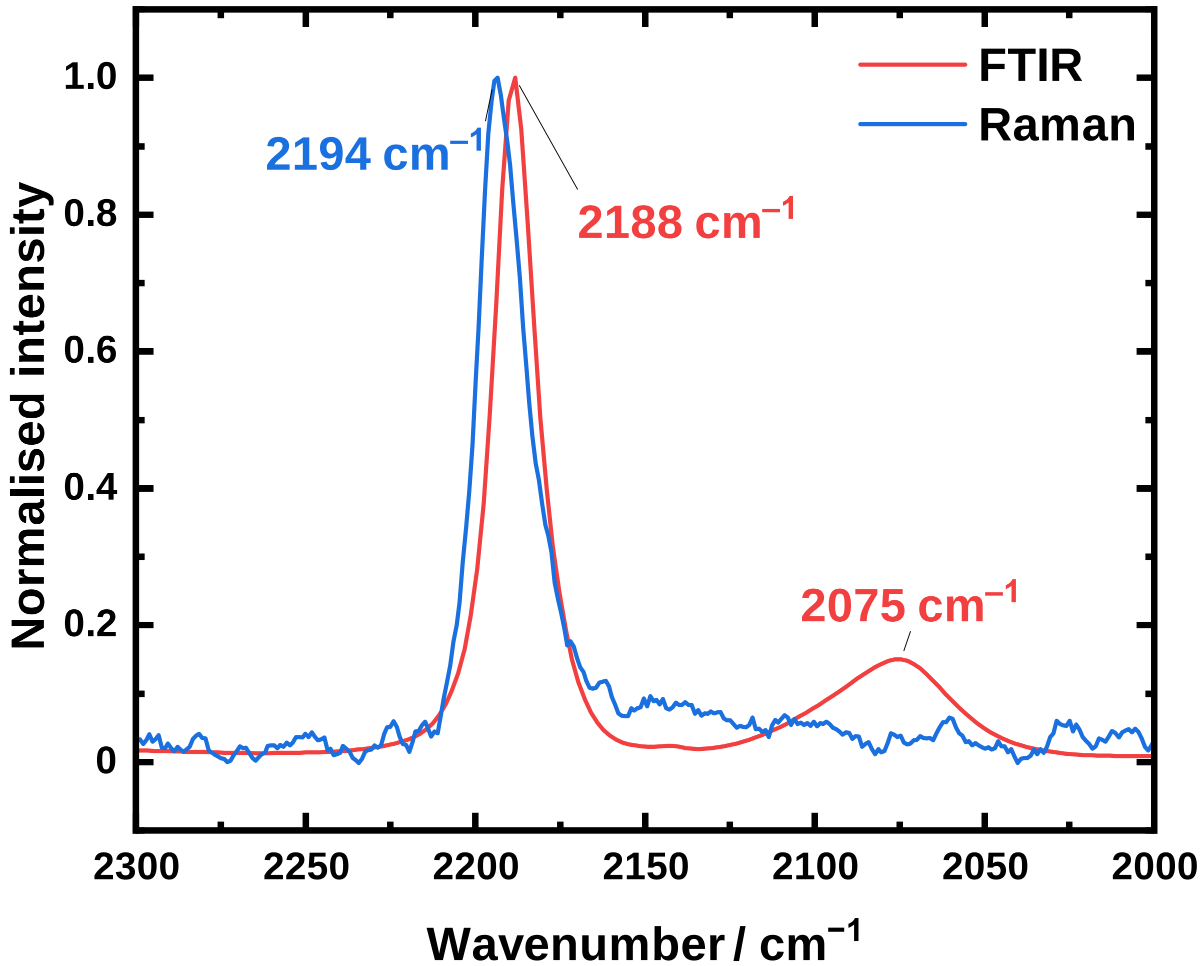

Fig. S2 Complementary vibrational spectra recorded for a single exposed Cr−Cr PBA film through FT-IR reflectance and inelastic Raman scattering using a 514 nm laser source.

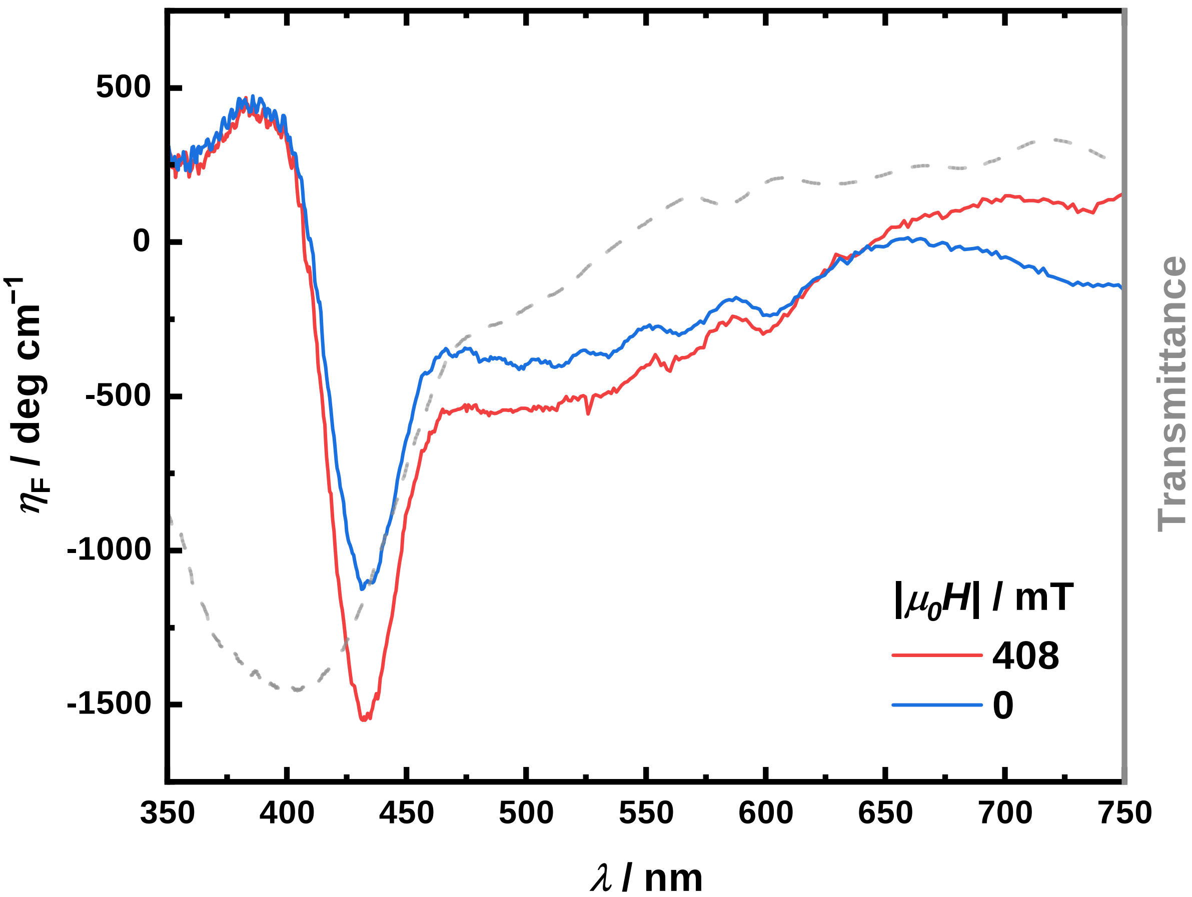

Fig. S3 Magnetic circular dichroism (MCD) spectrum recorded for the reduced Cr−Cr PBA film at 80 K with different applied fields (coloured solid lines, left axis) with overlaid static transmittance spectrum (grey dotted line, right axis). For $|\mu_0 H| = 0$ mT measurements, a 408 mT field is briefly applied before each acquisition to align the magnetisation of the film, but no field is applied during data collection.

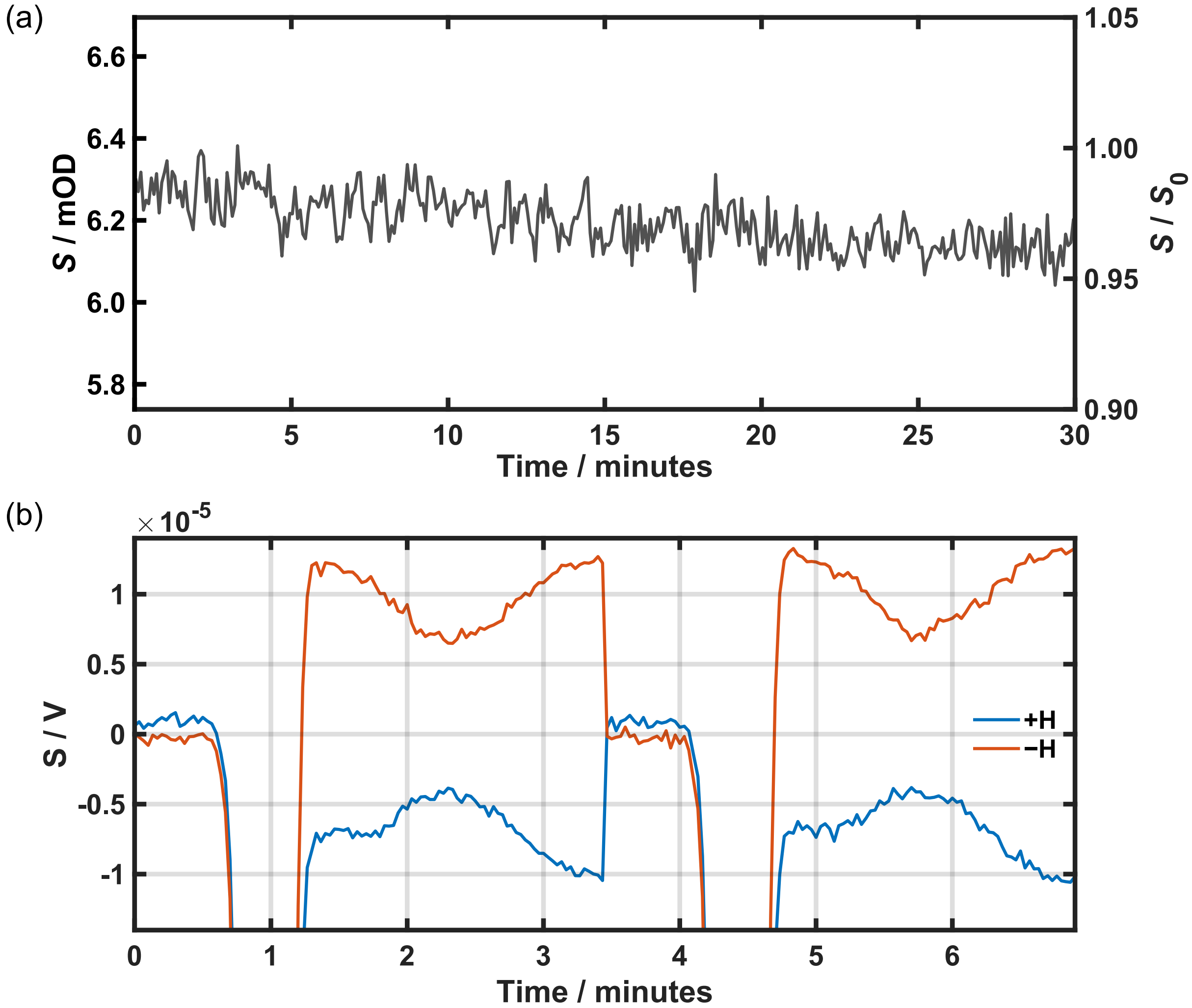

Fig. S4 Photostability of pump–probe response for transient transmittance (TT) and time-resolved magnetic circular dichroism (TR-MCD) measurements performed using an 800 nm pump of fluence 4.2 mJ cm^{-2}. (a) TT response observed in a 1 kHz 420 nm probe at fixed time delay upon prolonged photoexcitation at 295 K. (b) Consecutive TR-MCD traces observed in a 20 kHz 400 nm probe over time upon prolonged photoexcitation at 80 K.

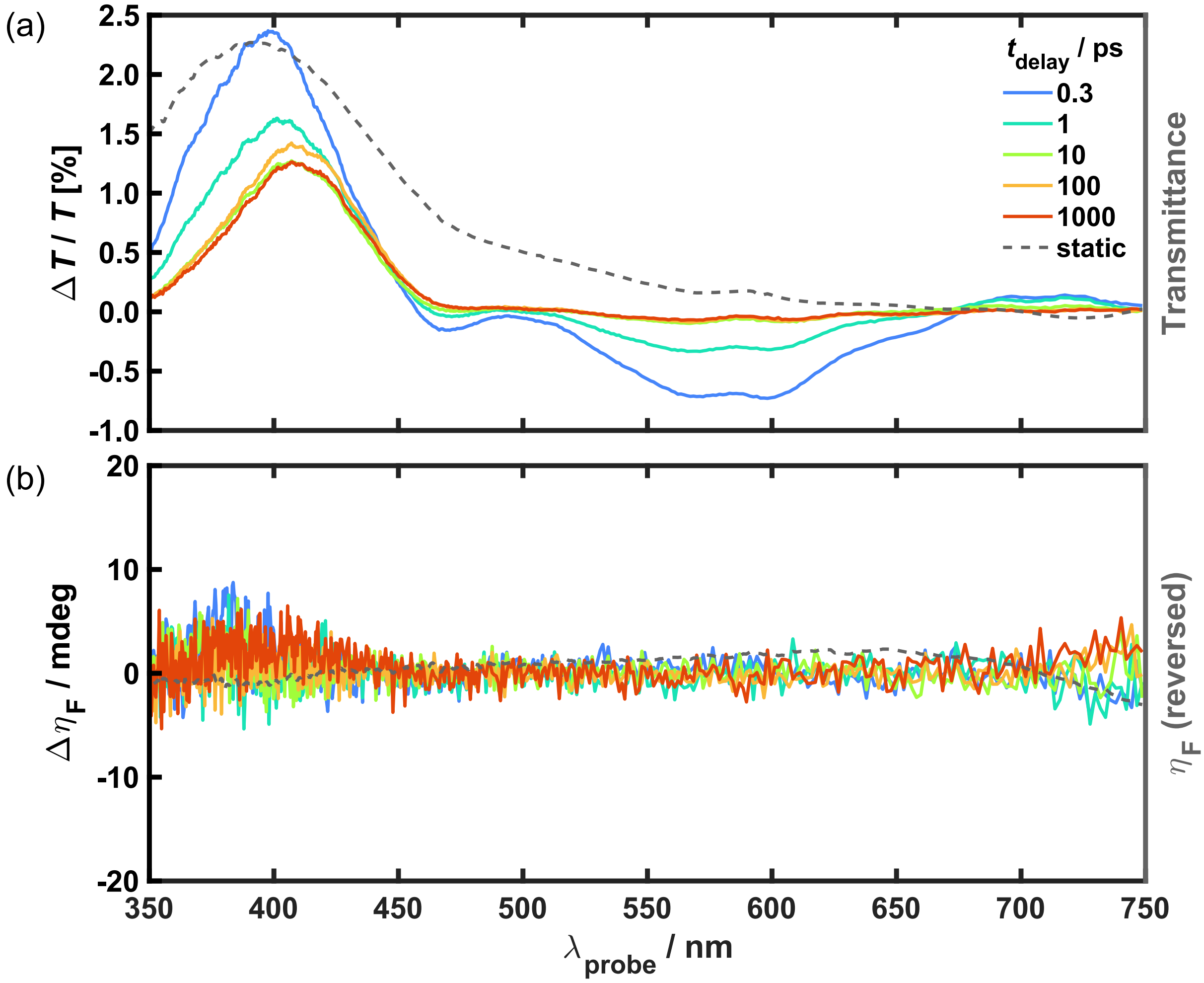

Fig. S5 Spectral-dependence of electronic and magnetisation dynamics at discrete t_{delay} in Cr−Cr PBA upon photoexcitation with an 800 nm pump of fluence 4.2 mJ cm^{-2} at 295 K under an applied field of 407 mT. (a) TT difference spectra (coloured solid lines, left axis) with overlaid static transmittance spectrum (grey dotted line, right axis). (b) TR-MCD difference spectra (coloured solid lines, left axis) with overlaid static MCD spectrum (grey dotted line, right axis). The static MCD is reversed along the y-direction to aid comparison to the TR-MCD.

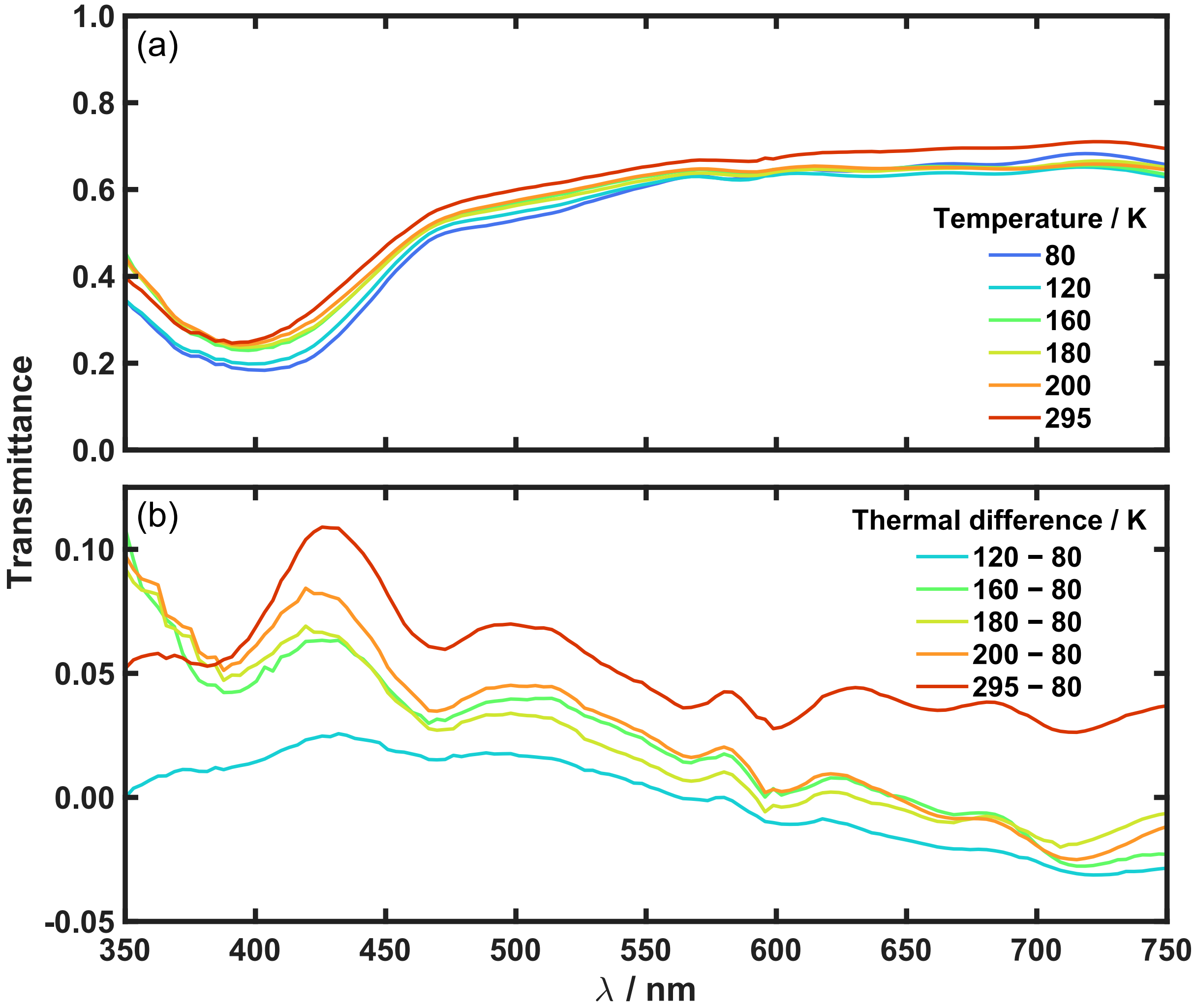

Fig. S6 Temperature-dependence in electronic spectrum recorded for the Cr−Cr PBA film using white-light supercontinuum as a light source. Top panel: UV-visible-NIR transmittance spectra recorded at six temperatures between 80 and 295 K. Bottom panel: Thermal difference spectra calculated to emulate temperature-induced changes observed upon heating the film from 80 K.

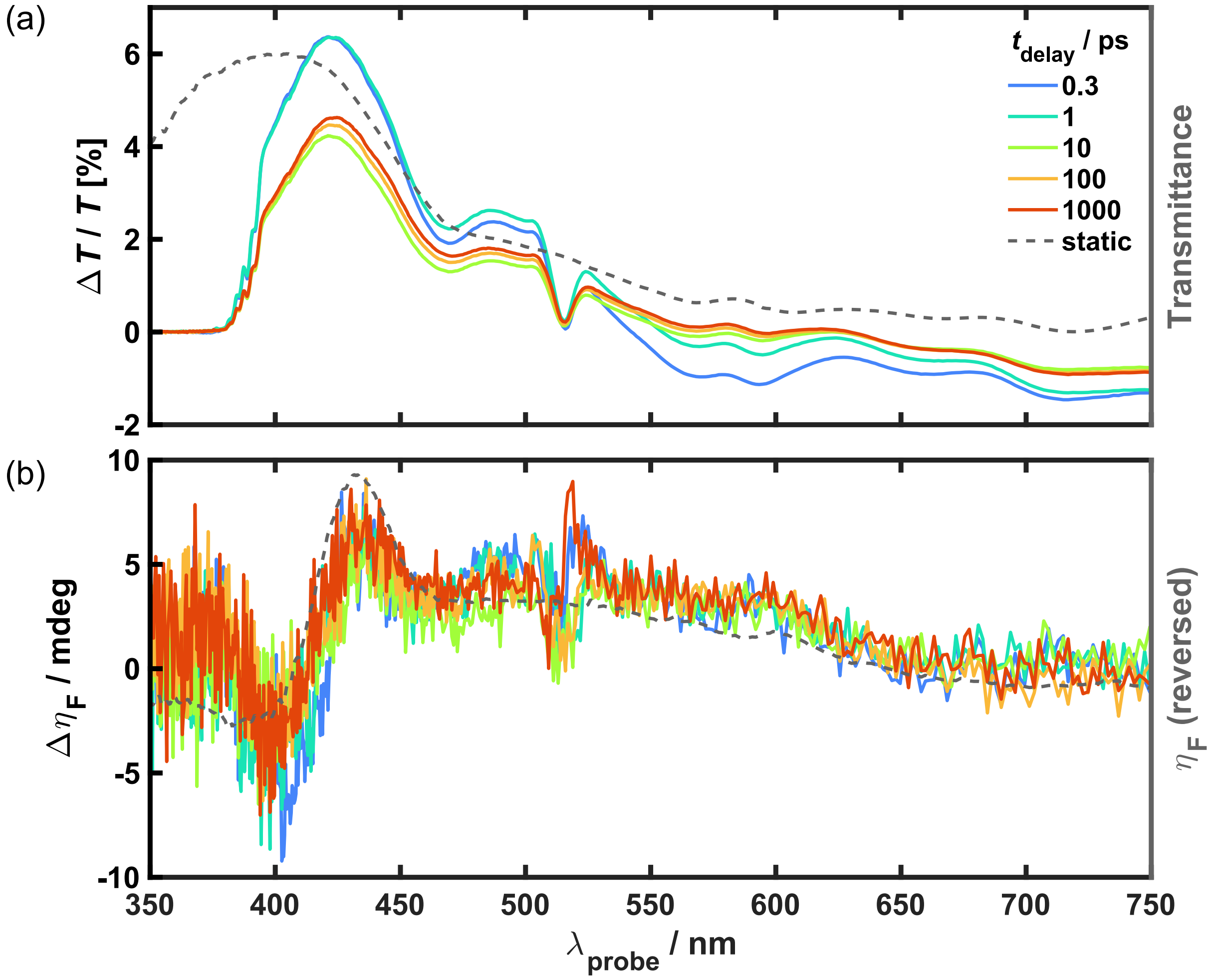

Fig. S7 Spectral-dependence of electronic and magnetisation dynamics at discrete t_{delay} in Cr−Cr PBA upon photoexcitation with a 514 nm pump of fluence 1.9 mJ cm^{-2} at 80 K under an applied field of 65 mT. (a) TT difference spectra (coloured solid lines, left axis) with overlaid static transmittance spectrum (grey dotted line, right axis). (b) TR-MCD difference spectra (coloured solid lines, left axis) with overlaid static MCD spectrum (grey dotted line, right axis). The static MCD is reversed along the y-direction to aid comparison to the TR-MCD. Note that the abrupt cut-off for $\lambda_{\text{probe}} < 400$ nm and dip at 514 nm arise from the use of a notch filter to block out the pump after the sample.

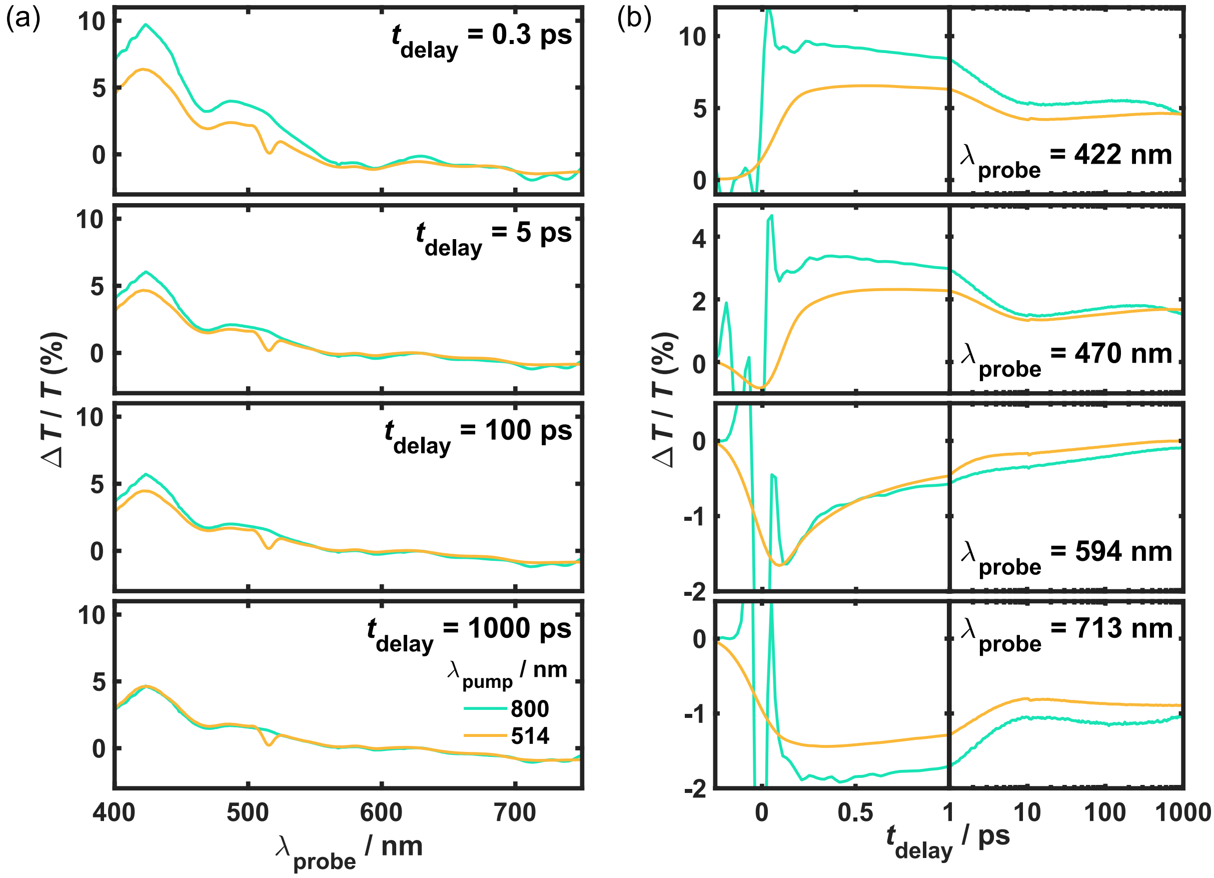

Fig. S8 Comparison of TT response observed upon photoexcitation at 800 nm (fluence 4.2 mJ cm^{-2}) and 514 nm (fluence 1.9 mJ cm^{-2}). The pump fluence for 514 nm excitation was selected to obtain the same level of response at longer t_{delay} as that observed for the 800 nm pump. (a) TT difference spectra recorded for finite time delays. (b) TT kinetic traces obtained for probe wavelengths of interest.