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Electronic Supplementary Information

for

Symmetry Breaking Charge Transfer and Intersystem Crossing in Copper Phthalocyanine Thin Films

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The excitation density for TA measurements is calculated as follows:

$$\rho = \alpha \cdot \frac{P_{in}}{E_\gamma} [cm^{-3}] \tag{1}$$

Where the absorption coefficient, α (Equation 2), depends on the measured absorption, which is wavelength dependent, *Abs*, in O.D., see Figure 1, and on the thickness of the sample, in this case, 50 nm:

$$\alpha = \frac{Abs(\lambda)}{l} \cdot 10^7 [cm^{-1}] \tag{2}$$

The incident power per pulse, P_{in} (Equation 3) is calculated from the measurement of the incident pump power P_{pump}, adjusted with a gradient neutral density filter, the laser repetition rate = 1 kHz, and the measured pump-beam radius, r:

$$P_{in} = \frac{P_{pump}[\mu W]}{RR \cdot \ \pi r^2} [J \cdot cm^{-2}\ per\ pulse] \tag{3}$$

The photon energy, E_γ (Equation 4), for each wavelength measured in nm, using Planck's constant and the speed of light:

$$E_\gamma = h \cdot \frac{c}{\lambda} [J/\gamma] \tag{4}$$

Table S1. Excitation density at each excitation wavelength for the α-CuPc thin film.

Wavelength (nm)	580	620	680	720
Ex. Density (cm^{-3})	$1 \cdot 10^{18}$	$1 \cdot 10^{18}$	$8 \cdot 10^{17}$	$9 \cdot 10^{17}$

Table S2. Excitation density at each excitation wavelength for the β-CuPc thin film.

Wavelength (nm)	580	620	680	720
Ex. Density (cm^{-3})	$2\cdot10^{18}$	$2\cdot10^{18}$	$7\cdot10^{18}$	$4\cdot10^{18}$

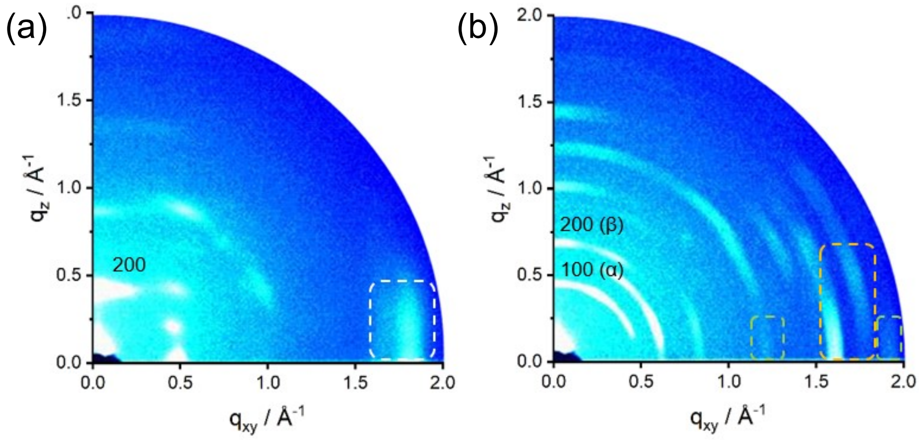

Figure S1. GIWAXS patterns of (a) α-CuPc (as-depositied) and (b) β-CuPc (annealed) thin films. Only the major reflection of the phases are assigned by the Miller index, while dashed boxes indicate reflections related to intracolumnar CuPc packing (white – α-herringbone, orange – α-brickstone, green – β-phase).

The as-deposited film reveals a characteristic α-herringbone structure (J. Am. Chem. Soc. 2012, 134, 14302−14305) with CuPc molecules arranged perpendicular to the substrate (Figure S1a). As indicated by the wide-angle reflections (white dashed box in Figure S1a), the molecules are in-plane shifted towards each other resulting in an interplanar distance of 3.45 Å and Cu-Cu distance of 3.75 Å. After annealing, the scattering intensities form arcs due to a broader orientation of the crystallites towards the surface (Figure S1b). Furthermore, the coexistence of two phases is identified based on the assignment of the reflections. New wide-angle reflections (orange dashed box in Figure S1b) are characteristic for the α-brickstone structure with interplanar and Cu-Cu distances of 3.49 Å and 3.85 Å, respectively, as well as a CuPc tilt angle of 75° with respect to the surface. Additionally, reflections for the β-phase are found in which the CuPc adapt a larger molecular displacement in the stacks resulting in Cu-Cu distance of 4.95 Å and interplanar distance 3.30 Å (green boxes in Figure S1b).

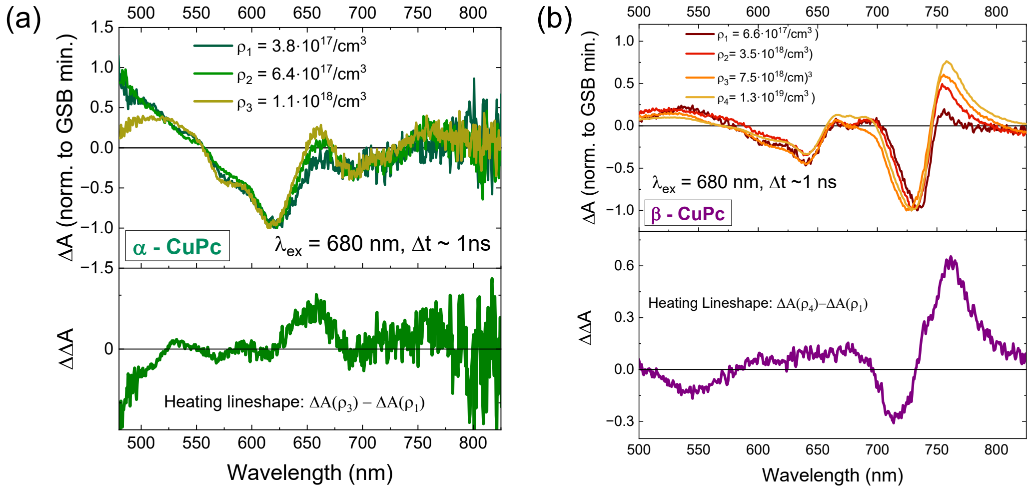

Figure S2. TA measurements with increasing excitation density are used to elucidate the ΔA signal that arises due to local heating effects for (a) α-CuPc and (b) β-CuPc thin films.

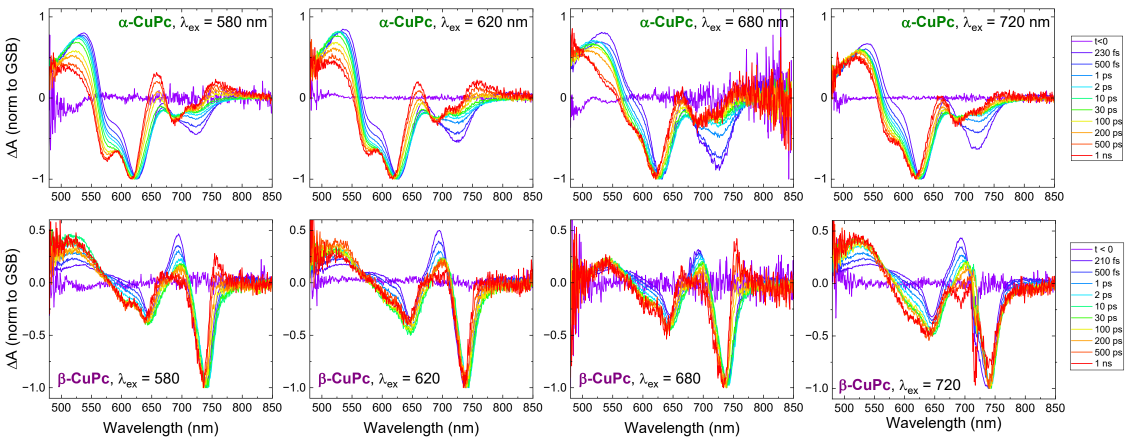

Figure S3. Normalised spectral traces at selected delay times for α-CuPc and β-CuPc thin films indicate that heating artefacts, evidenced by the blue shifting of the GSB and appearance of other features shown in Figure S1, appear later delay times (> 100 ps).

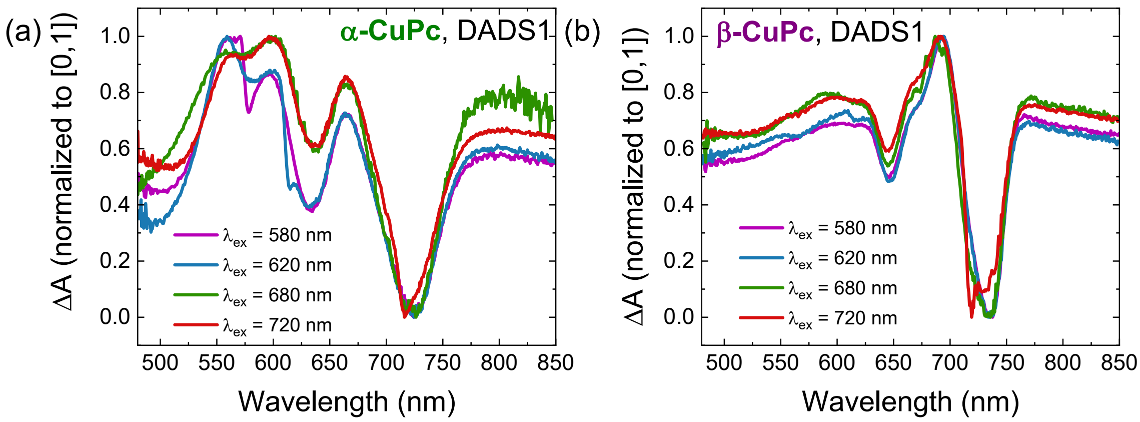

Figure S4. Comparison of Decay-Associated Difference Spectra for (a) α-CuPc and (b) β-CuPc thin films show an excitation dependent lineshape between 550-600 nm for α-CuPc that does not appear for β-CuPc

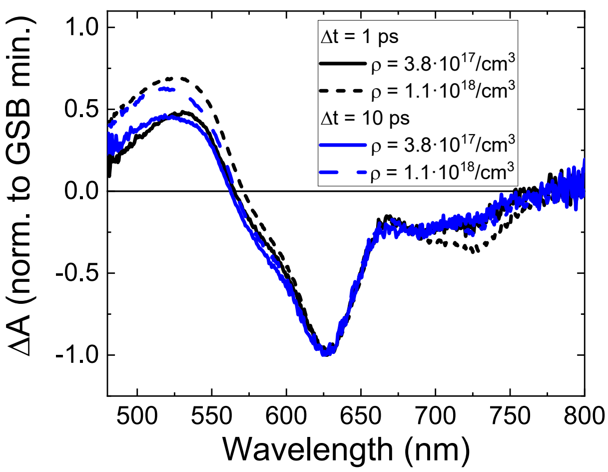

Figure S5. The spectral lineshape at Δt = 1 ps and 10 ps for α-CuPc at different excitation densities are similar, further confirming that the excitation wavelength dependent feature is not a heating artefact.