Electronic Supplementary Information for "Femtosecond to Nanosecond Excited State Dynamics of Vapor Deposited Copper Phthalocyanine Thin Films"

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I. THERMAL EFFECTS:

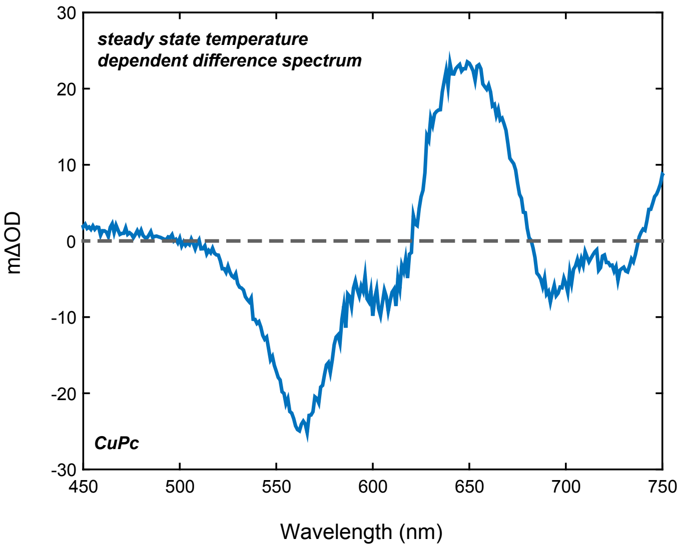

FIG. S1. The thermal difference spectrum resulting from subtracting the absorption spectrum of a 318 nm thick CuPc film at 56°C from that of the same sample at 26°C.

In solution pump-probe experiments excess thermal energy can be transferred to the solvent on the picosecond timescale which is usually spectrally silent in the visible region of the spectrum. However, neat films lack a thermal bath in which to deposit excess thermal energy on the picosecond timescale. Instead this energy will be dissipated on the nanosecond to microsecond timescale through heat transfer to the substrate.[1,2] What this means is that for experiments conducted on the ca. 1 ns timescale, the 'baseline' corresponding to the electronic ground state may not be a flat line centered at $\Delta OD = 0$. In order to understand what effect this may have in transient absorption experiments, we collected a steady state absorption spectrum near room temperature and subtracted it from a spectrum collected at elevated an temperature. These two spectra can be subtracted to give a thermal difference spectrum corresponding to the effect of thermal energy, and this is plotted in Figure S1. It was confirmed by cycling the temperature that there was no substantial hysteresis due to temperature induced 'aging'. This spectrum agrees well with the literature.[3]

Importantly, this thermal difference spectrum shows that the effect of thermal energy on the transient data is very weak at 470 nm, and at 532 nm the effect would be to generate a negative transient signal. The transient absorption experiments observed a sizable positive signal at both 470 nm and 532 nm and so these features are not due to thermal effects.

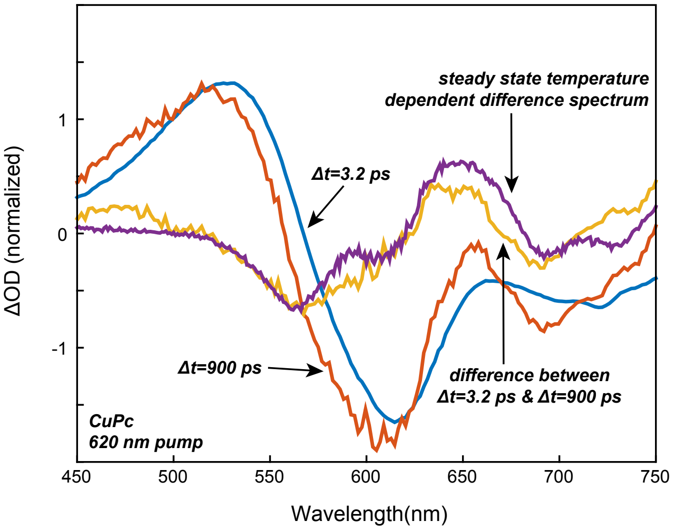

FIG. S2. Two time slices ($\Delta t = 3.2, 900$ ps) from a transient absorption experiment conducted on a CuPc sample are plotted; they have been scaled to have similar amplitude for the excited state absorption feature. The difference between these scaled spectra is shown overlaid with the scaled thermal difference spectrum for comparison. For (only) this experiment the relative polarization between the pump and probe were ca. 20° .

Although not important for the conclusions of the manuscript here we highlight the influence of the thermal effects on the time-resolved data. As an example, in Figure S2 we show two time slices for a CuPc film excited resonantly at 620 nm with a fluence that generates an excited state population ca. 5% of the molecular density. This high density causes annihilation to speed the recovery to the ground electronic state (normally for CuPc this would take many nanoseconds for monomolecular decay). The time slice at 3.2 ps (after the sub-picosecond intersystem crossing) and the time slice at 900 are scaled to have equal heights at the excited state absorption feature for comparison. It is clear that some spectral evolution has occurred during between these time points. These two spectra are subtracted and plotted next to a scaled thermal difference spectrum (see Figure S1). It can be see that the spectral changes associated with the annihilation are nearly identical to the spectral changes expected for heating of the film. If the heating effect were not considered then these spectral changes might be interpreted as being electronic in origin.

A similar picture can be made for the differences between the transient spectrum collected

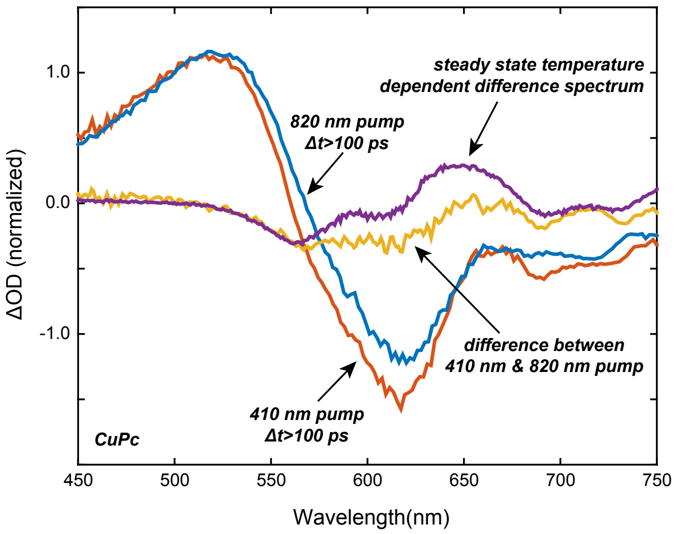

FIG. S3. Transient absorption spectra at $\Delta t > 100$ ps are plotted for a 820 nm and 410 nm pump; they have been scaled to have similar amplitude for the excited state absorption feature. The difference between these scaled spectra is shown overlaid with the scaled thermal difference spectrum for comparison.

using an 820 nm pump versus a 410 nm pump. Time slices from after 100 ps are plotted for these two experiments and scaled to the excited state absorption feature as above. Then these two spectra are subtracted and plotted next to a scaled thermal difference spectrum. Although the agreement between the thermal difference spectrum and the calculated spectrum is certainly not perfect, given that these two experiments were performed on different samples on different days with different pump conditions we find the data to be consistent with one another, thus, highlighting the importance of thermal effects on interpreting transient spectra of neat materials.

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