Reply to "On the observation of photo-excitation effects in molecules using muon spin spectroscopy"

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We reported [1] changes in the muonium (Mu) addition rate to different sites in 6,13-bis(tri(isopropyl)silylethynyl)pentacene (TIPS-Pn) in CH_2Cl_2 when it is photo-excited compared with the ground electronic state. Scheuermann and McKenzie report in a comment [2] that their independent analysis of the transverse-field (TF)-μSR and avoided level crossing (ALC)-μSR spectra in [1] indicate that there is no statistically significant effect of photo-excitation on this rate.

One of the main criticisms from Scheuermann and McKenzie [2] is that effective rate constants for muon addition in other smaller molecules are in excess of 10^9 $M^{-1}s^{-1}$, and that this is too large to be compatible with our interpretation of our TIPS-Pn data. For example, one would expect significant effects to amplitude when the muon -> muoniated radical conversion rate is between about 0.1 and 10 μs^{-1}, which would correspond to a rate constant between about 10^6 – 10^8 $M^{-1}s^{-1}$ in the TIPS-Pn concentration measured in our experiment (see supplementary information). We note that McKenzie et al. are assuming that the rate constant for this reaction in TIPS-Pn is the same as the smaller molecules, as this has not been measured in TIPS-Pn. We have provided (see supplementary information) a comprehensive set of data that all indicate that the effective rate constant for these reactions is below 10^9 $M^{-1}s^{-1}$, and probably between 10^7 - 10^8 $M^{-1}s^{-1}$, within the range required for our interpretation to be correct.

Scheuermann and McKenzie argue that Fourier-transformed TFμSR spectra presented in [1] cannot establish and quantify any effect of illumination with statistical significance. They were unable to reproduce some of the analysis presented by Wang *et al.*, [1] using a standard methodology for the interpretation of muonium chemistry experiments. As discussed in supplementary information Scheuermann and McKenzie [2] have fitted two overlapping ALC resonances to a double Lorentzian, where fit parameters will have significant covariance and there are insufficient points to reliably fit the number of parameters in their fits, resulting in significant uncertainties on the extracted parameters. We note that the TF fits by Scheuermann and McKenzie also appear to be all-parameter fits, which may be physically unrealistic. For example, the applied field in both light-on and light-off data is identical and so the frequency, amplitude and phase of the low-frequency component will have shared parameters.

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We agree, some of our data is challenging to analyze, and we already considered the alternative interpretation and analysis methods presented by Scheuermann and McKenzie. Wang *et al*. [1] as detailed in the supplementary information have demonstrated a set of analyses that are consistent across multiple μSR experimental geometries and techniques, with the key results agreeing with independent results from optical spectroscopy [3] following photoexcitation of TIPS-Pn. In particular there is a match between the decay rate of a triplet detected by optical spectroscopy [3], and that detected by μSR (Figure 2c in Wang et.al. [1] and 13a of the supplementary information), confirming μSR is measuring photoexcitation and the light-induced changes are not an artefact induced by data analysis.

We believe that the body of evidence indicates the initial conclusions and interpretation of Wang *et al*. [1] are correct, but that clearly further work is needed to develop the photoμSR technique, which is in progress.

References:

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3] B.J. Walker, A.J. Musser, D. Beljonne and R.H. Friend. Singlet exciton fission in solution. *Nature Chemistry* 5, 1019_1024 (2013).

The authors declare no competing interests.