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Temporal mapping of photochemical reactions and molecular excited states with carbon specificity

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Photochemical reactions are essential to a large number of important industrial and biological processes. A method for monitoring photochemical reaction kinetics and the dynamics of molecular excitations with spatial resolution within the active molecule would allow a rigorous exploration of the pathway and mechanism of photophysical and photochemical processes. Here we demonstrate that photo- μ SR, a pump-probe spectroscopic technique, can temporally and spatially map these processes with a spatial resolution at the single-carbon level in a molecule with a pentacene backbone. The observed time dependent light-induced changes of an avoided level crossing resonance demonstrates that the photochemical reactivity of a specific carbon atom is modified as a result of the presence of the excited state wavefunction. This demonstrates the sensitivity and potential of this new technique in probing the dynamics of molecular excitation and photochemistry.

Dynamics of molecular excited states govern photochemical reactions that are key to a phenomenal number of important industrial and biological processes. For example, molecules in living organisms are often exposed to solar radiation, and in the case of photosynthesis this light energy is captured to provide the energy that supports almost all life. Moreover, the effect of this solar radiation on biomolecules such as DNA plays an important evolutionary role^{1,2}. In the chemical engineering field, stereoselective synthesis enables the construction of a vast array of organic molecules with precise control over their three-dimensional structure^{3,4}, which is important in a variety of fields ranging from drug discovery to materials engineering. Photochemical reactions have a substantial impact on these fields by affording direct access to certain structural motifs that are otherwise difficult to construct⁵. For example, the malaria drug artemisinin is commercially produced with a key photochemical step⁶. In organic electronics the complex physics of excitations is critical to device function⁷⁻¹³. High efficiencies have been reached for both organic light emitting diodes (OLEDs) and organic photovoltaics (OPVs)¹⁴⁻¹⁷, yet a major barrier to the deployment of organic semiconductors is their functional lifetime¹⁷. For example, a recent study of the chemical reactivity of derivatives of anthracene and tetracene in the OLED environment indicates that free-radical chemistry is initiated after photo-excitation by homolytic bond dissociation reactions, which result in hydrogenation reactions¹⁸.

We have developed the experimental technique photo- μ SR¹⁹ so that it can now measure the spatial distribution of electron density in the molecular excited state at any given time. Whilst this technique has previously been used to study excitations predominantly in semiconductors^{19,20} and a limited number of solutions of organic molecules²¹, no spatial information has been gained up until now. By making use of Avoided Level Crossing (ALC) spectroscopy, whose resonance positions are specific to individual carbons, we demonstrate that crucial information on the fundamental photochemical and excited state processes can be obtained. We demonstrate this new application of the technique in a 10 mM solution of the organic semiconductor 6,13-bis(tri(isopropyl)silylethynyl) pentacene (TIPS-Pn) (Figure 1a), dissolved in O₂-free dichloromethane (DCM). We present convincing evidence that muonium is able to map the time evolution of the excited state wavefunction on the pentacene backbone of the molecule, as a direct result of its sensitivity to electron density when reacting. We demonstrate that reaction of muonium with this extended aromatic system probes the relative levels of chemical reactivity of carbon atoms after excitation with light, and that this can be tracked as a function of time.

Photo- μ SR

In our photo- μ SR experiment, a 25 Hz, \sim 10 ns pulsed Nd:YAG laser was used to excite the TIPS-Pn molecules in solution with a wavelength of 532 nm and a pulse energy of 91 mJ. The light-pump muon-probe measurements were carried out with the light flash triggered to arrive T_L before the muon pulse, to excite the TIPS-Pn molecules prior to the arrival of the muons, as depicted in Figures 1b and c. The changes to the photochemical reaction rates as a result of the excitation can then be probed with muonium, a chemical analogue of hydrogen (see below). The 25 Hz laser in combination with the 50 Hz muon pulse enabled light on/off data to be gated to alternate histograms, thus averaging out any long-term changes to the sample and accelerator profile. Further technical details can be found elsewhere^{19,22} and in the Supplementary Material.

When implanted into many materials including organic solvents, the positively charged muons can either thermalize as diamagnetic species or form hydrogen-like muonium atoms, Mu²². Mu is thought of as a light pseudo-isotope of the hydrogen atom, in which an electron orbits a muon

(μ^+) nucleus, which is 0.11 the mass of H and behaves chemically like an H atom²²⁻²⁶. Due to the unsaturated bonds and aromatic rings that are present, muonium can react with TIPS-Pn with almost identical chemistry to a hydrogen atom creating an electrically neutral radical. There are three species of muon in our sample, a diamagnetic and two types of paramagnetic species: the unbound solvated species with a hyperfine coupling (HFC) constant of order 4.4 GHz, and a number of muoniated radicals, which have a significantly lower HFC constant for the muon and other nuclei in the molecule that are dependent on their local environment.

Indeed, it is these differences in HFCs that depend on the muon's local environment which give us spatial sensitivity. The unpaired electron wavefunction in a radical overlaps with the nuclei and gives a series of hyperfine coupling constants for all the nuclei with non-zero spin, which are generally much lower than for the individual free atoms. In the simpler case of gases, liquids or solutions only the isotropic parts of the coupling constants need be considered. When a magnetic field is applied parallel to the muon's initial spin polarisation, the spin energy levels are split by the Zeeman interaction. At certain fields, the combination of Zeeman and hyperfine interactions cause cross-relaxation between the muon and one of the other nuclei, and a so-called avoided level crossing (ALC) resonance.^{22,27,28,29}

These resonances are usually plotted as the "integral asymmetry" - the average muon polarisation weighted by the muon lifetime, and take the form of relatively sharp dips. The amplitude of the integral ALC resonance depends on the hyperfine coupling of both muon and nucleus. In many aromatic molecules each radical species has one dominant resonance due to the α -proton. The amplitude and width are also affected by relaxation and other dynamics, and the formation rate and probability of that species. ALCs from different radical species caused by different addition sites of the muonium will generally be at quite different fields, so they can be measured individually. Importantly, one of the main drivers of the relative amplitude of the various ALC resonances is the reaction kinetics associated with muonium bonding. That is itself driven by the electrostatic potential, which of course can be quite different when the molecule is in the ground state compared to an excited state. We show that our photo- μ SR experiment can spatially probe the molecular excited state and its role in determining reactivity of the molecule, all at an individual atom level. Moreover, by changing the pump-probe delay time, T_L , temporal information is obtained as the transient excited species evolves with time.

Light induced effects on ALC spectra

Figure 2a shows the ALC spectra taken for muonium bound to carbons 1, 2 and 4 in TIPS-Pn at $T_L = 130$ ns. The laser and muon pulse are sufficiently separated to ensure that photo-ionisation of muonium or muoniated radicals could not occur³⁰. Figure 2b shows the ALC from muon-electron and muon-proton (α -proton) HFCs predicted from ab-initio density functional theory (DFT) calculations, which can be used to assign the bonding site for each ALC resonance. The site assignment is in the inset. Further details of these DFT calculations can be found in the Supplementary Material. It is immediately clear that photo-excited changes to the spectra are evident for sites 1 and 2 but not site 4. The largest changes are evident at site 2, with a clear increase in amplitude, or area of the ALC, as well as a small shift in the ALC minima (potentially as a result of a HFC change). There could be an increase in the width of the lines for both sites 1 and 2, although this is difficult to quantify since these ALCs overlap. Figure 2c inset shows the light-induced change in asymmetry as a function of T_L , at two fixed fields (indicated by the arrows in Figure 2a), corresponding to sites 2 and 4 (indicated by the arrows in Figure 1a).

There are two components present corresponding to ALC spectral changes at site 2, with different signs and timescales, that are not present at site 4. The 6.5 μs lifetime of the triplet molecular excited state is clearly evident in the slower component - incontrovertible evidence that muonium is capable of measuring triplet excited states. The ALC amplitude of this component is reduced in the triplet state. The faster component, with an increased ALC amplitude, has a timescale of approximately 1 μs .

Light-induced changes to the ALC spectra can take many forms, for example additional resonances could appear or ALC positions could shift, due to the multiple unpaired spins on the molecule¹⁹. There could be a change in hyperfine coupling constant due to a structural or conformational difference³¹, an increased electron spin relaxation or exchange³²⁻³⁴, or a modification of the muonium reaction rate for a given carbon³¹. It is extremely unlikely that a conformational change or multiple unpaired spins can account for this data, as the ALC at around 300 mT for site 4 is identical for the light on and off cases. Both conformational or unpaired spin changes would modify the muon-electron and/or proton-electron isotropic hyperfine coupling (HFC) for all adducts³¹. For the same reasons, we also discount localized heating as result of absorption of the light, since a relatively small change in temperature is known to significantly alter the position of the ALC for site 4 (see Figure S4 in the Supplementary Material). We also believe that electron spin relaxation and/or spin exchange cannot account for these changes, as it is known to affect all ALCs in a similar fashion in the solid state^{32,33}, there is no associated increase in relaxation rate and it cannot account for all of the features in the time dependent data (see the Supplementary Material). To explain our observations, one must invoke the mechanism of radical formation from the solvated muonium. Muons thermalize very quickly, in less than 1 ns,²² with the final result in fully saturated organic solvents being a mixture of solvated muonium and diamagnetic muons. The muonium then chemically reacts with the unsaturated or aromatic solute molecules, and if this final stage is not sufficiently prompt, then a number of features are observed in the data, which evolve with the reaction rate. These features, discussed below, are not present in the other candidate mechanisms mentioned above.

Interpreting the ALC spectra

In a weak transverse field (WTF), the energy difference between the two triplet transitions $|1/2, 1/2\rangle \rightarrow (|1/2, -1/2\rangle + |-1/2, 1/2\rangle)/\sqrt{2}$ and $(|1/2, -1/2\rangle + |-1/2, 1/2\rangle)/\sqrt{2} \rightarrow |-1/2, -1/2\rangle$ are equal and relatively small, resulting in low-frequency Rabi oscillations^{22,27}. The WTF spectra shown in Figure 3a and b, demonstrate a clear triplet precession signal (fast oscillation) superimposed on the precession from the diamagnetic muons (slow oscillation). The triplet precession results from muonium that stop in the unbound state, either in the SiO₂ window or the solvent. For muoniated radicals, the magnetic field at which the Zeeman splitting becomes non-linear (i.e the two triplet transitions have a different energy) is significantly lower and the proton coupling splits the triplet energy difference. Given there are multiple radical states with different muon-electron and proton-electron HFC, the resulting signal is rather more complex, comprising of a superposition of multiple beating signals. We note that this will be also true for muonium addition to the triple bond of the sidegroup, despite it not having an α -proton (see Supplementary Material). Moreover, the larger dynamics present in bound muonium and the nuclear HFC significantly relaxes the triplet precession. All of these effects conspire together to make the radical triplet precession signal in a WTF all but invisible. However, changes in the solvated muonium amplitude, present if there is a light induced change in reaction rate, are readily observable in the data upon fitting the spectra to $A(t) = A_{\text{mu}}\cos(\omega_{\text{mu}}t + \phi_{\text{mu}})\exp(-(\sigma_{\text{mu}}t)^2) + A_{\text{u}}\cos(\omega_{\text{u}}t + \phi_{\text{u}})\exp(-$

$(\sigma_{\mu}t)^2$). This represents a Gaussian damped precession of the triplet muonium (first term) and spin precession in the applied field of the diamagnetic muons (second term), from which the light induced change in the triplet precession asymmetry, $A_{\text{WTF}} = A_{\text{mu(on)}} - A_{\text{mu(off)}}$, is extracted. Figure 3c shows A_{diff} with $T_L = 130$ ns, for several WTFs. All show a reduction in asymmetry of the triplet precession signal under photo-excitation, and this reduction appears to be field independent within error. This change is also present in the Fourier transforms of the data, an example of which is shown in Figure 3d (see Figure S5 in the Supplementary Material for all the Fourier transforms). This is clear evidence that there is an overall reduction in the amount of solvated muonium present following photo-excitation, which is consistent with an increased reaction rate of the solvated muonium with the molecule following excitation.

This conclusion has some implications about the timescales. If the reaction rate is comparable with the solvated muonium hyperfine frequency, then the shape of the LF repolarisation curve is strongly governed by the reaction rate, as the muon partially exchanges spin polarisation with the electron before forming the radical. However, the ALC amplitude is almost reaction rate independent, since at high fields the muon's spin should be nearly or fully repolarized. Clearly, we are not in this fast regime. If, on the other hand, the reaction rate approaches the lifetime of the muon (in excess of ~ 100 ns), then the ALC amplitude is dependent on the reaction rate, as some muons will decay and be measured before they have a chance to react. Moreover, in this slow limit, there will be a clear two-step signature in the ground-state LF repolarisation curve and only a weak light-induced effect in the intermediate field region of the LF repolarisation. Both of these features are very clear in Figure 4a and b. Importantly, the data shown in Figure 4a corresponds to a 10 mM solution of TIPS-Pn in DCM using a standard Titanium cell mounted on an Aluminium plate, on the EMU spectrometer at ISIS. Because of the materials used in this cell, the two-step repolarization curve clearly evident in Figure 4a *must* be from the TIPS-Pn or DCM, and not the surrounding environment. This is strong evidence for either an entirely unreacted fraction of muonium, or a relatively slow reaction rate of muonium with the molecule.

Bringing all of the above information together, the light induced changes to the ALC spectra in Figure 2a are mainly related to a change in the reaction rate of the muonium with the molecule, specific to carbon 2. Whilst the mechanism of photodegradation in TIPS-Pn has not been fully clarified^{35, 36}, it previously been inferred that TIPS-Pn undergoes a photoinduced inter-molecular 4 + 4 cycloaddition via a π -dimerization process³⁵. However, we see little evidence for the reaction rate of muonium with site 4 being enhanced by excitation, probably because muonium chemistry is a good model for radical reactions, whereas dimerization of TIPS-Pn is an electrocyclic reaction.

Quantum chemical calculations were used to explore the electrostatic potentials that promote or inhibit molecular interactions, and to identify regions of the TIPS-Pn molecule with higher chemical reactivity. DFT was used with the B3LYP functional and cc-pVDZ basis set embedded in the Gaussian package³⁷. After geometry optimization, the atomic charge distribution within the molecules along with its electronic volume was determined by a population analysis of the molecular orbitals. The surface enclosing 99% of the electronic density was calculated on a grid from the molecular orbital coefficients. The molecular electrostatic potential (MEP) was mapped³⁸ onto this surface (Figure 4c) for both ground state and triplet state. The potential becomes significantly less negative around the bond between carbons 1 and 2 when the triplet excited state is present, as a result of the electron density becoming more dispersed around the end ring of the backbone of the molecule. This is most easily observed by plotting the difference

between the MEPs for T_1 and S_0 in the top panel of Figure 4c, which shows that there is a reduction in the electron density between carbons 1 and 2 of approximately 5%. There are also changes to the electrostatic potential in the region of carbon 4, with a clear shift of electron density towards the center of the molecule from the bond between carbons 4 and 3. The change to carbon 4 is roughly symmetrical - such that there is no large change in the overall electron density of the two bonds around carbon 4. This, coupled with steric hindrance of the side groups, may explain why there are no light-induced effects to the ALC associated with carbon 4. In addition to the changes to the electric potential governing chemical reactivity, there may also be a spin effect. It is likely that the muoniated molecule is in a doublet state, provided the spin of the muonium electron is opposite to the spin of unpaired electron already present. It is currently unknown what effect this will have on reactivity. The quartet state would result in the muon electron residing in a higher energy orbital, which would probably reduce the overall reactivity.

Molecular excited states and photochemical timescales

We now discuss the timescales presented in Figure 2c. Recently, it has been shown that triplet-triplet dimers formed in TIPS-Pn dissolved in chloroform have an emission lifetime of approximately 220 ns³⁹. Whilst the 1 μ s photo- μ SR signal and this 220 ns dimer lifetime differ by a factor of over 4, molecular interaction probabilities are strongly dependent on both concentration and solvent, as demonstrated by work on photodegradation³⁶, so it is feasible that dimerisation processes are responsible for this timescale. Careful study of the transient absorption spectra reported by Walker et al.³⁹ for a concentration of 0.075 mol l⁻¹ reveals a clear feature around 1.6 eV, also with a lifetime of approximately 1 μ s. The onset of aggregate absorption in TIPS-Pn is 1.65 eV. Given this and the MEP discussed above, we suggest that the 1 μ s photo- μ SR component is related to an ‘excimeric’ process – i.e a species comprising two molecules, one in the ground state and the other in an excited state. The different electron densities of the ground state and triplet would probably promote a Coulomb initiated ‘excimer’ state in TIPS-Pn, which presumably then leads to the eventual 4+4 cycloaddition at carbon 4, and a net increase in the muonium reactivity at carbon 2 while this state exists. Nonetheless, further study of this transient state with a 1 μ s lifetime is necessary to properly identify it and its significance.

The 6.5 μ s signal matches the triplet lifetime³⁹ and is therefore conclusive evidence that excited state processes can be measured with muoniated radicals with intra-molecular spatial resolution. Its amplitude has the opposite sign to the 1 μ s signal, suggesting that it is directly related to a reduction in the reactivity of the muonium with the molecule, as a result of the reduced electron density in the carbon 2 bonds when the molecular excited state is present, as shown by the MEPs in Fig. 4c. This result, demonstrating that the time dependence of the excited state can be probed with an intra-molecular spatial resolution, is in itself quite remarkable. In principle, it should also be possible to image the time-dependency of charge transfer states, in those systems where charge separation occurs in the excited state. Given the MEPs shown in Figure 4c, it would be interesting to probe the central carbon atoms in TIPS-Pn, but unfortunately the relevant muonium bonding sites are blocked by the steric hindrance of the side groups.

Conclusions

We have demonstrated that reaction of muonium with an extended aromatic system can probe the relative levels of susceptibility of individual carbon atoms to chemical reaction upon excitation with light, and that this can be tracked as a function of time. We have presented

evidence that a possible excited state with a 1 μ s lifetime could be important to the photochemical degradation of TIPS-Pn in solution. This demonstrates the use of laser pumped μ SR and avoided level crossing resonances to gain insight into photochemical reactivity; clearly the technique has significant potential in other aromatic systems. We note that in TIPS-Pn, there are no polar species that would result in charge transfer states, so the changes to the electrostatic potential are relatively small. It would be interesting to extend this technique to molecules with such polar groups, where much larger changes to the electrostatic potential may be present, perhaps by either chemical modification of the TIPS-Pn backbone or by studying a known donor-acceptor molecule.

There is a second component that matches the triplet lifetime, 6.5 μ s. This is strong evidence that muonium is able to map the time evolution of the excited state wavefunction on the molecule as a direct result of its sensitivity to electron density when reacting. This provides spatial resolution for studying excited state dynamics. To our knowledge, the experimental approach used here is the only one with this degree of temporal combined direct intra-molecular spatial sensitivity; for example, typical resolution in other mapping techniques are in excess of ten nm^{40,41}. It may also be possible to extend the time window down to nano- or pico-seconds with future technical developments. An experimental demonstration of these fast dynamics, we believe, will be an important step in the technique and for a suitably chosen molecule, significant insight may be gained into the very fast photo-chemical and excited state processes at the molecular level.

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Author contributions KW and PM contributed equally to this work. KW, PM, KY, JSL, FLP, JH, LS, MW, NAM, SZ, PH and AJD performed the experimental work. KY, PM, JSL and AJD designed, built, tested and commissioned the photo- μ SR spectrometer (to be described fully elsewhere). PM, KY, JSL, LN, DJD, KS, IW, PH and AJD set-up the experimental equipment for the work reported here. KW, JSL and AJD analyzed and interpreted the musr data. KW and AM performed the DFT calculations. JEA, PH and AJD interpreted the implications of the results. Everyone contributed to writing the paper. AJD conceived the research and managed the project.

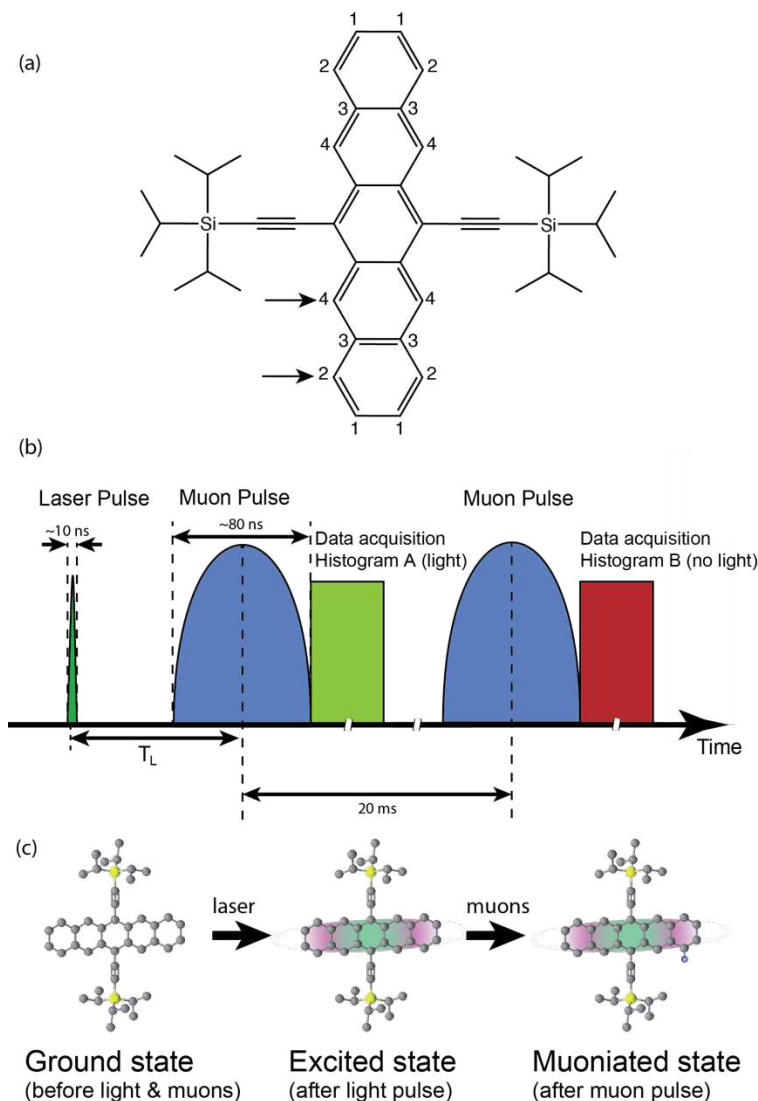


Fig. 1: A schematic illustration of the molecule under investigation and the experimental setup. (a) The molecular structure of TIPS-Pn. The labels are referred to in the text. Sites 1,2 and 4 can support muonium bonding. All similarly numbered sites are equivalent, by symmetry. (b) The pump-probe pulse structure in our experiments. The laser pulse (dark green) is triggered to arrive prior to the muon pulse (blue), and the delay time between the pulses, T_L , is controllable. The muon pulses are separated by 20 ms, which is determined by the ISIS synchrotron intrinsic frequency of 50 Hz, whereas the laser is fired at 25 Hz. The data is then gated to different histograms, depending on whether a laser pulse directly preceded the muon pulse or not (c) The different stages of the molecule during the experiment. TIPS-Pn starts out in the ground state, without a muon probe present. Upon excitation with light, an excited state is formed as indicated by the green and pink shading, which is subsequently probed with a muonium that bonds to one of the carbons.

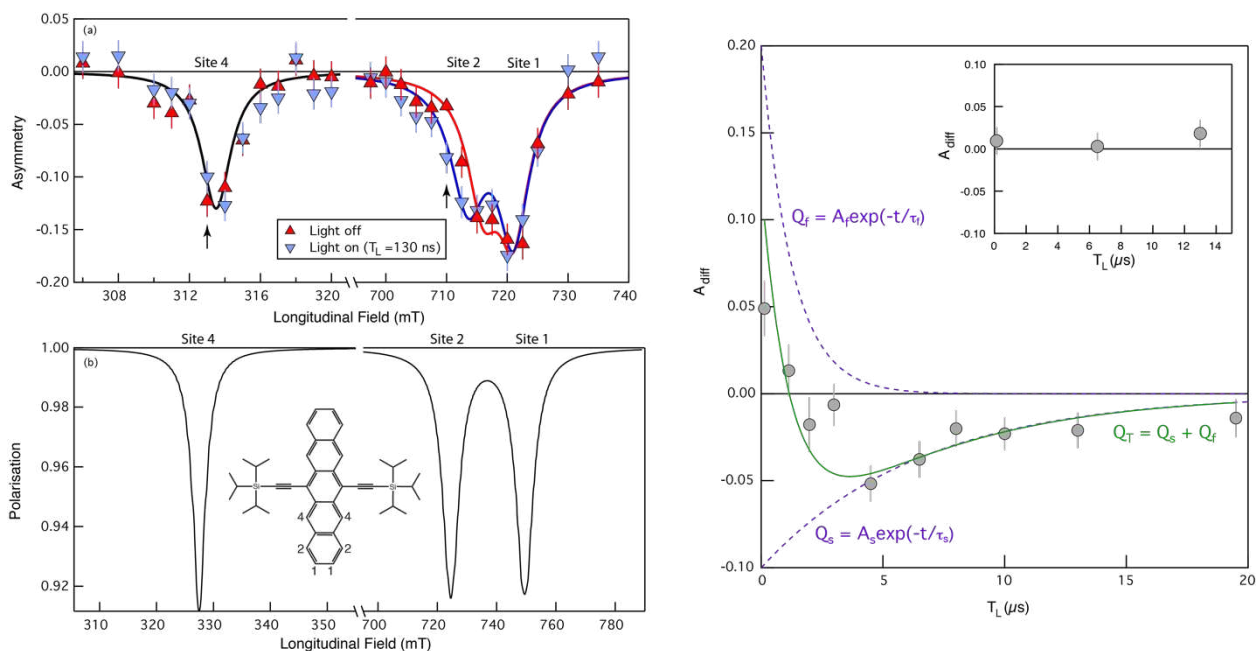


Fig. 2: The time-dependent ALC measurements. (a) ALC spectra with light off (red) and light on (blue) with a pump-probe time delay of 130 ns. There is a clear light-induced change in shape of the two ALCs corresponding to sites 1 and 2, manifesting itself predominantly as a shift in position and an increase in amplitude/area, with the largest changes evident for site 2. The arrows correspond to the fixed fields that were measured as a function of T_L . (b) Predicted lineshapes from DFT calculations (see Supplementary Material), from which site-assignments can be made. The ALC at around 310 mT corresponds to site 4, whereas there are two ALCs that partially overlap at around 710 mT, corresponding to sites 1 and 2. (c) The pump-probe delay time dependence of the change in amplitude of the ALC at 710 mT, $A_{\text{diff}} = A_{\text{off}} - A_{\text{on}}$. There are two timescales present, one at $\tau_f = 1 \mu\text{s}$ and a second at $\tau_s = 6.5 \mu\text{s}$, with opposite signs to the amplitudes A_f and A_s . Lines are guides to the eye, with the lifetimes fixed to values from transient photoabsorption measurements at 1.6 eV and 1.25 eV for τ_f and τ_s , respectively.³⁵ We note that the statistical error bars as plotted are significantly larger than any systematic errors in this measurement, which is reinforced by the similarity between the two lifetimes derived from the photomusr data, and those extracted from the transient photoabsorption data. Inset: Corresponding data on the ALC at 314 mT, where there appears to be no change in the ALC as a function of time.

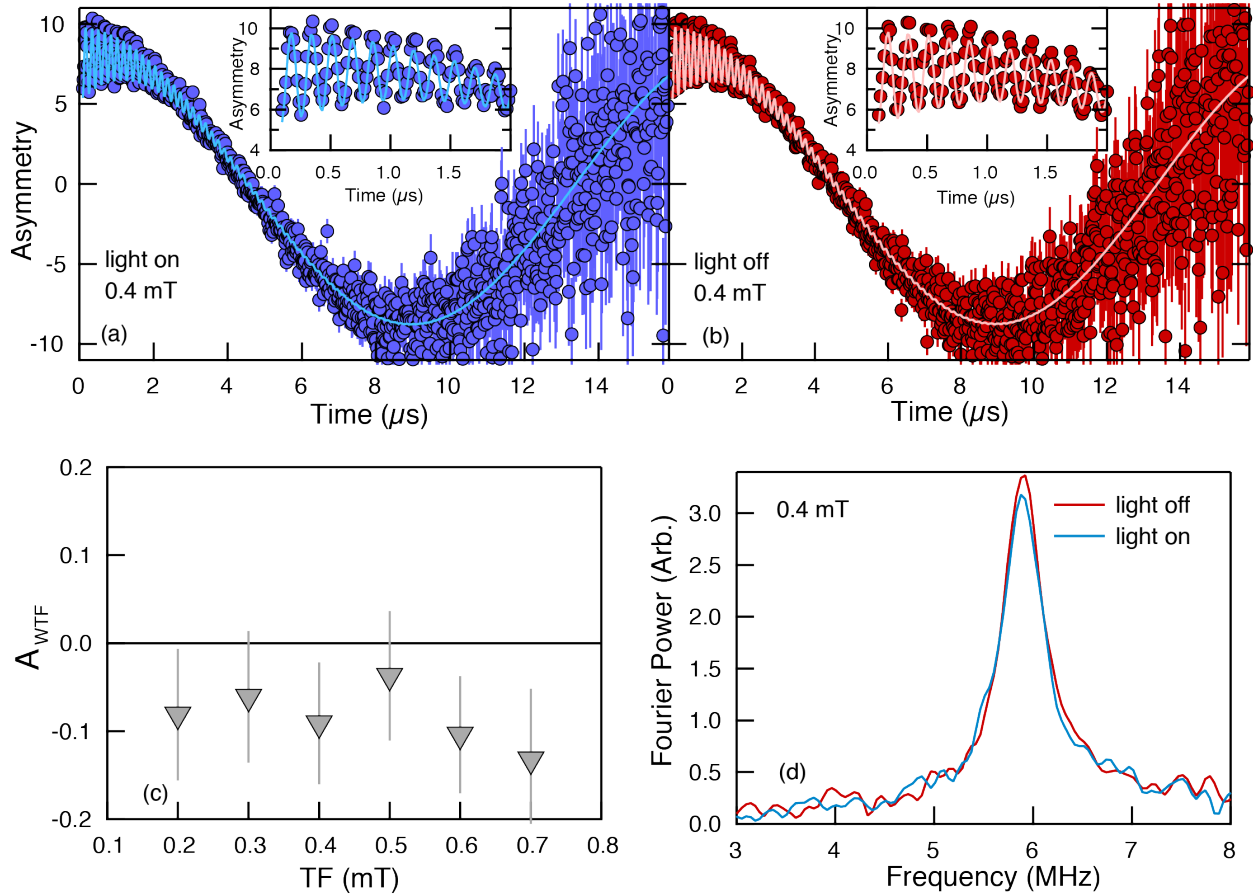


Fig. 3: A variety of muon measurements undertaken to understand the increase in amplitude of the ALC at low times. (a-b) Weak transverse field data for light on (blue) $T_L = 130$ ns and light off (red), demonstrating that diamagnetic muons (slow precession; main panel) and unbound solvated muonium (fast triplet precession; insets) are present. The data have been fit to a two-component model (see text) to extract light induced amplitude changes to the two components. (c) The light induced change in amplitude of the triplet precession, $A_{\text{WTF}} = A_{\text{mu(on)}} - A_{\text{mu(off)}}$. At all fields measured, there is a net reduction in solvated muonium when excitations are present, and it appears to be field independent. (d) Fourier transforms of the data shown in panels a-b, further demonstrating a light induced change in amplitude, commensurate with a loss of solvated muonium.

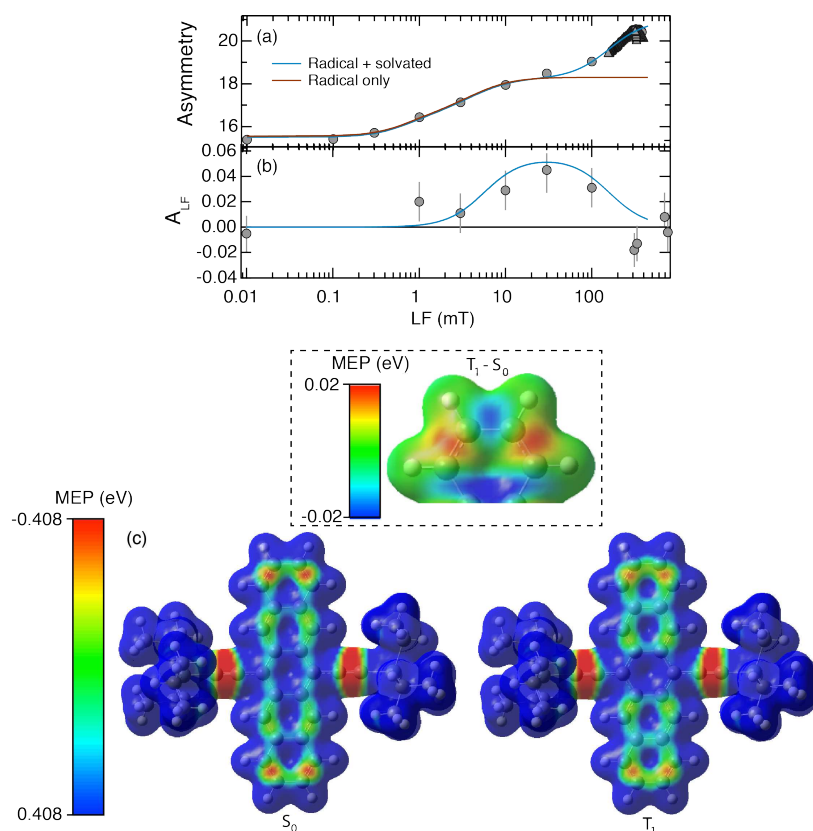


Fig. 4: Consistency checking with ground state muon measurements (a) Longitudinal field repolarization data taken on the EMU spectrometer at ISIS in the ground state, using a well-characterised sample cell made from Ti. The data shows a clear two-step repolarization curve, corresponding to a radical fraction and solvated muonium. The lines correspond to the expected repolarization curve for just a radical (red) and a combined radical and solvated muonium state (blue). HFCs of 80 MHz and 4463 MHz were used for radical and solvated muonium, respectively. (b) The difference between the LF asymmetry for light on and off, $A_{LF} = A_{on} - A_{off}$, for $T_L = 130$ ns, using the HiFi spectrometer and the laser sample cell. A very small change at intermediate fields is present, which is consistent with a change in reaction rate dynamics in the slow limit or overall population reduction of the solvated muonium (see text). The line is a guide to the eye, representing the functional form expected from light-induced changes. (c) The electrostatic potential map of the ground state S_0 and triplet excited state T_1 generated from DFT calculations (see text). On the end of the backbone, the charge is more spread when the triplet is present, resulting in a reduction in charge around the bond between carbons 1 and 2. This is most easily demonstrated by plotting the difference between T_1 and S_0 , which is shown in the top-center of panel (c). Here, the colour-scale is amplified by a factor of 20, such that the red regions demonstrate a reduction in electron density of about 5%, and blue corresponds to an increase in electron density of about 5%.