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Paramagnetic probes in an organic semiconductor: μ SR and DFT calculations of the Mu adducts of Alq₃ and 8-hydroxyquinoline

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ABSTRACT

It has been claimed that longitudinal field muon spin relaxation (LF- μ SR) experiments on the organic semiconductor (OSC) tris-(8-hydroxyquinoline)aluminum(III) (Alq₃) have measured electron hopping rates of $\sim 10^{12} \text{ s}^{-1}$, while density functional theory (DFT) calculations suggest that electron hopping between a muoniated radical and a neighboring molecule is energetically unfavorable and that the LF- μ SR experiments were probing muoniated radicals with localized spin density. We have performed avoided level crossing muon spin resonance (ALC- μ SR) and transverse field muon spin rotation (TF- μ SR) measurements on Alq₃ and 8-hydroxyquinoline (8hq), which is meant to model the muoniated radicals present in Alq₃ when they are not in an OSC. These are supplemented by benchmarked DFT calculations. The ALC- μ SR and TF- μ SR spectra of 8hq and Alq₃ are best explained by Mu adding to all six secondary carbons of the quinolate rings with roughly equal yields and localized spin density. There is no evidence in the TF- μ SR spectrum of Alq₃ for the formation of radicals with muon hyperfine coupling constants of 23 or 91 MHz as reported earlier by others. Our measurements support the view that there is localized spin density on the molecule to which Mu is covalently bound and the muon is not a passive probe in organic systems as it can be incorporated into radicals that have different electronic structures to the parent compounds. The muoniated radicals in Alq₃ are more short-lived than in 8hq, which could be due to interactions with mobile electrons in the OSC, but with electron spin flip rates on the order of $\sim 10^7 \text{ s}^{-1}$.

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I. INTRODUCTION

Throughout the history of the muon spin rotation, relaxation, and resonance (μ SR) technique, there have been questions concerning whether it is accurately probing the material or whether the perturbations caused by the muon stopping in the sample give rise to distorted views of the local environment. Whether it is an

“innocent” probe or not depends on what material is being studied. The most well-known example of muons being a perturbation is in semiconductors such as GaAs where the muon is not probing the pristine local environment around it but instead forms bond-centered muonium (Mu), where there is hyperfine coupling to the unpaired electron it has brought with it.¹ Another example is muons in Pr₂Sn₂O₇, a rare earth pyrochlore, where the presence of the

muon changes the crystal field around the rare earth ion and results in the muon probing something very different from the pristine crystal.² In many chemical systems, muons are undoubtedly a perturbation because they form Mu, which can react with unsaturated bonds to produce a muoniated radical. Muoniated radicals have a very different electronic structure to the parent diamagnetic compound. These radicals can be used as local probes of materials when studying dynamics of a particular component such as a cosurfactant in bilayers or micelles,^{3–5} but whether they can be used to study electron hopping is controversial due to the different electronic structure. The μ SR technique and its applications in the study of free radicals have been recently reviewed.^{6,7} In this paper, we consider whether muons are innocent probes in organic semiconductors (OSCs).

OSCs are materials having tremendous technological applications. Tris(8-hydroxyquinoline)aluminum(III) (Alq_3) is an OSC that is one of the most frequently used low-molecular weight materials for organic light-emitting devices (OLEDs).⁸ Alq_3 consists of an aluminum atom with three bidentate 8-hydroxyquinolate (8hq) ligands in an octahedral geometry (Fig. 1). In the crystal, there is good π - π orbital overlap between ligands of different molecules along the c axis, and this results in highly one-dimensional motion of

charge carriers. μ SR measurements on Alq_3 were reported in 2008.⁹ There, it was assumed that Mu adds to Alq_3 to give multiple types of muoniated radicals (Mu-Alq_3) with an average isotropic muon hyperfine coupling constant (hfcc) or A_μ of 425 ± 20 MHz, based on the repolarization curve. The signals due to these radicals were not observed in the transverse field muon spin rotation (TF- μ SR) spectrum at 0.25 T. Instead, two types of radical with much smaller muon hfccs (23 ± 1 and 91 ± 1 MHz) were observed at low temperature (10 K) but not at 290 K. The inset in Fig. 3 of Ref. 9 shows the 10 K FFT spectrum and compares it to the 290 K longitudinal field (LF) decoupling behavior. These signals were not assigned. Longitudinal field muon spin relaxation (LF- μ SR) spectra were obtained as a function of an applied longitudinal magnetic field. The muon spin polarization relaxed slowly and it was not obvious which relaxation function should be used to fit the spectra. The authors hypothesized that the relaxation of the muon spin in the longitudinal field was due to long-range diffusion of the unpaired electron, which was introduced by the reaction of Alq_3 with Mu. The LF- μ SR spectra were then analyzed using the Risch-Kehr (RK) function,¹⁰ which was developed for systems where there is long-range diffusion of the unpaired electron, such as in *trans*-polyacetylene.^{11,12} It is important to note that other relaxation functions could also have resulted

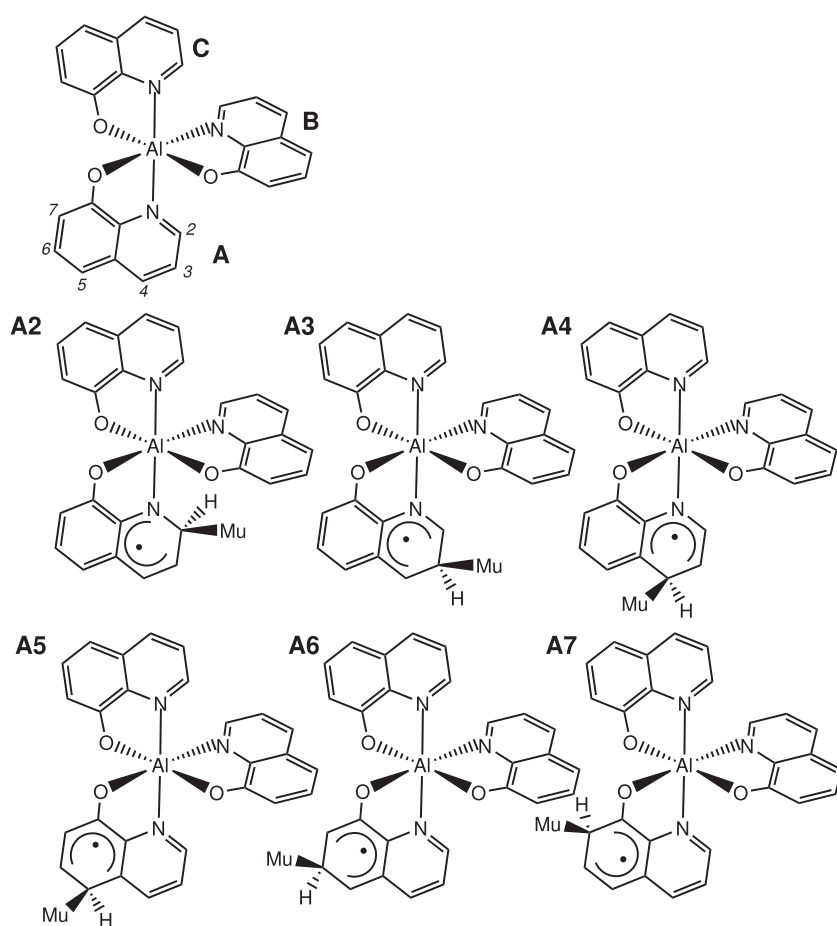


FIG. 1. Structure of the meridional isomer of tris(8-hydroxyquinoline)aluminum (III) (Alq_3) with the numbering of the positions on the A ligand and the structures of the most likely Mu adducts of the A ring. Radicals with similar structures will form by Mu addition to the B and C rings of Alq_3 .

in comparable fits of the spectra. The magnetic field dependence of the RK relaxation parameter led to the conclusion that the unpaired electron was hopping at the rate of $(1.4 \pm 0.2) \times 10^{12} \text{ s}^{-1}$ at 290 K. The interest in these measurements stems from the claim that μSR could be used to measure the intrinsic hopping rate of an electron in an OSC with very low concentrations of carriers due to the feature of self-generation of carriers by muon implantation.¹³ There is also the additional advantage that these measurements are not susceptible to disorder-induced bottlenecks present in conventional mobility measurements due to the muon being a local probe.

One can only obtain sensible information from an LF- μSR spectrum if one uses a relaxation function based on a physically realistic model.¹⁴ The problem is that sometimes different relaxation functions, which imply different microscopic behavior in the material, can fit spectra equally well. One can often not distinguish between different models based on the quality of the fit. This is the Achilles heel of the LF- μSR technique and is worst when one is analyzing spectra with slowly relaxing signals as in Alq_3 . The preceding analysis assumed that the muon just supplies the excess electron and is an innocent observer as the electron diffuses through the sample [Fig. 2(a)].

A different model has been proposed to explain the μSR experiments on Alq_3 ; rather than being a passive probe, the muon is a significant perturbation and the muoniated radicals that are formed have different electronic structures to Alq_3 . The structures of the muoniated radicals formed by Mu addition to Alq_3 are shown in

Fig. 1. Addition of Mu preferentially occurs at secondary unsaturated carbons rather than tertiary carbons,¹⁵ so it was assumed that Mu addition to each ligand of Alq_3 should produce six types of substituted muoniated cyclohexadienyl radical. Mu is distinguishable from H, so Mu addition leads to a center of chirality at the methylene carbon of the radical formed.¹⁶ Enantiomers give rise to identical spectra in magnetic resonance, but the chirality of Alq_3 breaks the degeneracy and makes it possible to distinguish between the diastereomers formed by Mu addition of different sides of the ligand rings. The result is that there are 36 distinguishable radicals (3 ligands \times 6 addition site \times 2 orientations). Density functional theory (DFT) calculations at the UB3LYP/6-31G(d,p) level of theory showed that the muoniated radicals have a very different electronic structure to the parent compound Alq_3 and it is energetically unfavorable for electron transfer in either direction between Alq_3 and the muoniated radical (ranging from 4.09 to 5.68 eV) [Fig. 2(b)].¹⁷ This implies that the unpaired electron is localized on the molecule where Mu is covalently bound.

As a way to distinguish between the “innocent” muon and strongly interacting muon models, the muon and methylene proton hfccs for the Mu adducts of Alq_3 , which are proportional to the unpaired electron spin density at the nucleus $[|\psi(0)|^2]$, were obtained from DFT calculations reported in 2010.¹⁷ Resonances can be observed in the avoided level crossing resonance spectrum (ALC- μSR) and the resonance fields (B_{res}) are related to the hfccs. Two types of resonances are typically observed; they are characterized by the selection rule $\Delta M = 0$ and ± 1 , where M is the sum of the

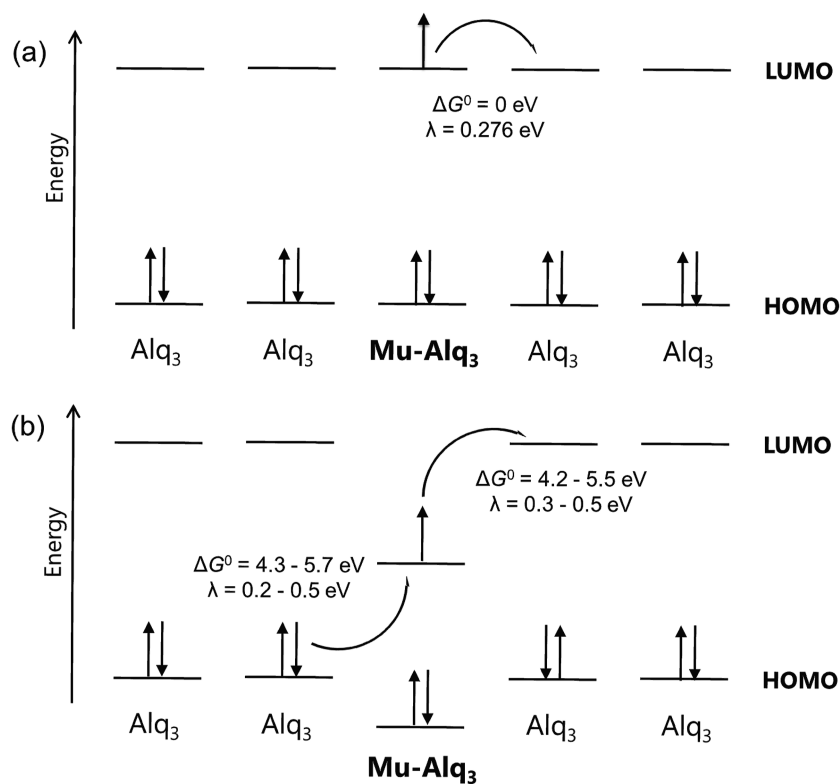


FIG. 2. (a) Muon as a passive observer. The Gibbs energy for electron transfer, ΔG^0 , is 0 and the reorganization energy for electron transport, λ , was calculated by Lin *et al.*¹⁸ (b) Muon as a perturbation; the energy levels of the muoniated radical are different from those of the parent compound. ΔG^0 and λ for electron transfer to and from the muoniated molecule calculated by McKenzie [UB3LYP/6-31G(d,p)].¹⁷ The singly occupied molecular orbital lies between the HOMO and LUMO of Alq_3 . The large ΔG^0 and λ values indicate the unpaired electron is localized on the molecule bound to the muon.

m_z quantum numbers of the muon, electron, and nuclear spins. The resonances are referred to as Δ_0 and Δ_1 resonances, respectively. The Δ_1 resonance field is given by

$$B_{\text{res}}^{\Delta_1} = \frac{A_\mu}{2\gamma_\mu} - \frac{A_\mu}{2\gamma_e}, \quad (1)$$

where γ_μ and γ_e are the muon and electron gyromagnetic ratios, respectively. The Δ_1 resonance is only observed when the radical is undergoing anisotropic motion or very slow isotropic reorientation, such as in a solid. The Δ_0 resonance field is given by

$$B_{\text{res}}^{\Delta_0} = \frac{1}{2} \left[\frac{A_\mu - A_X}{\gamma_\mu - \gamma_X} - \frac{A_\mu + A_X}{\gamma_e} \right], \quad (2)$$

where γ_X is the nuclear gyromagnetic ratio. Δ_0 resonances in the solid state tend to be much broader than Δ_1 resonances and, thus, smaller in amplitude. An example of this would be the Mu adducts of [2.2]paracyclophane where Δ_0 resonances were not observed even though the Δ_1 resonances were very strong.¹⁹ Based on the DFT calculations in Ref. 17, multiple Δ_1 resonances were predicted in the ALC- μ SR spectrum of Alq_3 between ~ 0.8 and 1.7 T. The observation of Δ_1 resonances in this field range with a full-width-at-half-maximum of ~ 0.1 T would be incompatible with an electron hopping at the rate of $(1.4 \pm 0.2) \times 10^{12} \text{ s}^{-1}$ over a number of molecules. This assertion is supported by simulations performed using the Quantum Monte Carlo simulation program (Fig. 3).²⁰ The simulations were performed on 10 molecules, one of which has Mu covalently bound; when the unpaired electron is on this molecule, there is a nonzero muon hfcc (isotropic muon hfcc = 250 MHz and dipolar muon hfcc = 10 MHz), and when it is on the other molecules, A_μ is zero. The Δ_1 resonance broadens substantially for electron hop rates of 10^6 – 10^7 s^{-1} and disappears when the electron hop rate is comparable to the isotropic muon hfcc. A new resonance forms at 1/10th the magnetic field of the original resonance when the electron hop rate is much larger than A_μ and is due to the unpaired spin density being equally distributed over the ten molecules. Electron hopping at $\sim 10^{12} \text{ s}^{-1}$ in a system containing a larger number of molecules would lead to the resonance going to zero field and disappearing as the unpaired electron spin density is distributed over a large number of molecules and would tend to zero at the muon.

In 2013 ALC- μ SR measurements were performed on Alq_3 at 10 and 300 K.²¹ The ALC- μ SR spectra were modeled using the Quantum Monte Carlo simulation program.²⁰ It was claimed that both the isotropic and dipolar muon hfccs as well as electron spin relaxation rates of five types of muoniated radical could be determined from modeling the spectra.²¹ We contend that it was not possible to determine these 20 parameters from overlapping resonance with only ~ 70 data points, especially with the errors that were reported. Nevertheless, the observation of multiple overlapping resonances between ~ 1.0 and 1.6 T appears to validate the calculations of McKenzie.¹⁷ However, in several recent reviews, Nuccio *et al.*²² and Wang *et al.*²³ have cast doubt on the calculations of McKenzie and extolled calculations that were reported in the Ph.D. thesis of Willis.²⁴ Wang *et al.* note that “only two of the eight known radical states are in good agreement with experimentally derived values. The remaining six

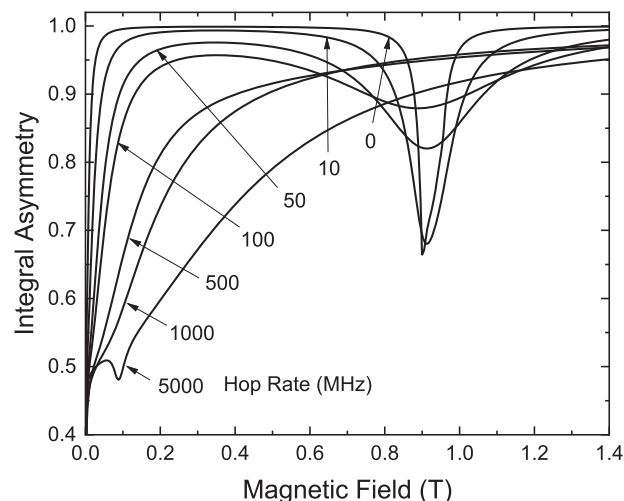


FIG. 3. Simulated ALC- μ SR spectra for electron hopping between 10 molecules where Mu is bound to one. There is a nonzero muon hfcc (isotropic muon hfcc $A_\mu = 250$ MHz and dipolar muon hfcc $D_\mu = 10$ MHz) when the unpaired electron is on the same molecule as the muon and zero hyperfine coupling when the electron is on one of the other nine molecules. The curves correspond to different electron hopping rates between adjacent molecules. The resonance is a Δ_1 resonance.

are either not predicted to be present or there are significant differences (of up to 40%) in the experimentally derived and theoretically predicted hfccs” and “benchmarking of the DFT methodology used, and it could be that these discrepancies could be minimized if a more thorough investigation was carried out.” We contend that it is more important to look at the pattern of the predicted and measured hyperfine couplings rather than whether there is exact agreement in the values.

It was claimed that the calculations reported by Willis were closer to the experimental values; however, these calculations used a demonstrably inferior computational method, specifically the semiempirical PM3 for geometry optimization. Curioni *et al.* found the PM3 method significantly overestimated the Al–N bond lengths and underestimated the Al–O bond lengths while calculations with the BLYP density functional were much closer to the experimental values.²⁵ The calculations reported by Willis did not account for the light mass of the muon on the hfccs, which increases the muon hfcc by $\sim 28\%$ for the $\text{C}_6\text{H}_6\text{Mu}$ radical.²⁶ The claim of better agreement with experimental values can be considered accidental at best, especially given the over-parameterized fits.

The goal of this paper is to characterize the muoniated radical states in Alq_3 and determine whether the observed spectra are consistent with localized spin density or rapid electron hopping. We have chosen to study the muoniated radicals formed by Mu addition to the quinolate ring when they are not in an OSC, and so would not expect rapid electron hopping. Ideally, we would study isolated Alq_3 molecules, but Alq_3 is not sufficiently soluble in any suitable solvent for μ SR measurements. Instead, we studied the 8hq ligand on its own and obtained μ SR spectra and performed DFT calculations. 8hq is not an OSC like Alq_3 , but the resulting radicals formed by Mu addition to 8hq will have very similar structures to the Mu adducts of Alq_3 (Fig. 4). We obtained an ALC- μ SR spectrum of 8hq from

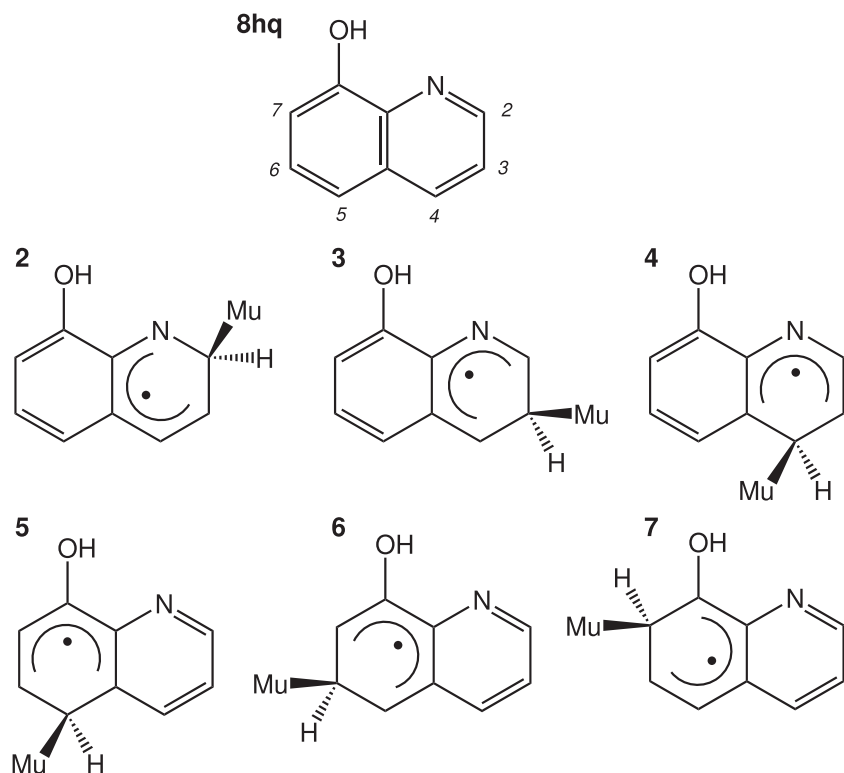


FIG. 4. Structure of 8-hydroxyquinoline (8hq) with the numbering of the positions on the aromatic ring and structures of the radicals produced by Mu addition to the secondary aromatic carbons of 8hq.

0 to 2.5 T and a high-statistics TF- μ SR spectrum at 1.45 T. We calculated the hyperfine coupling constants of the possible muoniated radicals with a larger basis set [UB3LYP/6-311+G(d,p)], accounted for vibrational averaging effects, and extensively benchmarked the calculations against similar muoniated radicals. We have compared the results on 8hq with improved μ SR spectra and DFT calculations of Alq₃. We have obtained a higher-quality ALC- μ SR spectrum of Alq₃ at 298 K over a wider magnetic field range (0–3.4 T) than previously reported and high-statistics TF- μ SR spectra at 0.25, 1.45, and 3.0 T. We have also calculated the isotropic and dipolar hfccs of the Mu adducts of Alq₃ in the same manner as the Mu adducts of 8hq.

The ALC- μ SR and TF- μ SR spectra of 8hq and Alq₃ are consistent with the radicals produced by addition to the six secondary carbons on the quinolate ring being formed in approximately equal amounts. This should be contrasted with radicals formed in the liquid state, where there is a clear preference for the lower energy products.¹⁵ The radicals were observed in the TF- μ SR spectra, although this generally required short time windows for the Fourier transform as the radicals, particularly in Alq₃, have large spin relaxation rates. The muoniated radicals with muon hfccs of 23 ± 1 and 91 ± 1 MHz reported by Drew *et al.* were not observed.

This paper conclusively demonstrates that the muoniated radicals formed in Alq₃ have localized spin density and suggest that the model proposed by Drew *et al.* involving electron hopping at rates of $(1.4 \pm 0.2) \times 10^{12} \text{ s}^{-1}$ is incorrect. This is likely the case as well for other OSCs studied by μ SR, such as Spiro-DPO.²⁷ This does not mean that muoniated radicals do not provide information about OSC. The broadening of the ALC resonances in Alq₃ due to electron

spin flips of $\sim 10^7 \text{ s}^{-1}$ could result from spin-exchange reactions between the muoniated radical and mobile carriers in the OSC and this should be investigated further.

II. EXPERIMENTAL

8hq and Alq₃ were purchased from Sigma-Aldrich and used without further purification. Alq₃ was encapsulated in a packet made of 25 μm silver foil measuring $1 \times 1 \text{ cm}^2$. This packet was placed on a silver backing with Apiezon N grease and held in place with a thin film of x-ray Mylar. 8hq was encapsulated in an Al sample cell with a thin Ti foil window.

ALC- μ SR measurements on 8hq and Alq₃ at 298 K were performed using the HELIOS spectrometer on the M15 beamline at TRIUMF. The spin polarization was antiparallel to the muon momentum. Both samples were mounted in a cold-finger cryostat, which was inserted axially in the HELIOS spectrometer. The ALC- μ SR spectra were obtained by scanning the magnetic field with steps of 20 mT and are the average of multiple scans. TF- μ SR measurements were made with the spin polarization rotated by 90° to the muon momentum. The magnetic field was calibrated at several points within the range of the ALC- μ SR spectrum by measuring the precession frequency of diamagnetic muons.

ALC resonances were observed on a nonlinear background that is due to the changes in the beam spot with applied field and field-dependent positron trajectories. The main background was accounted for by running the silver backing plate and fitting this spectrum with a sixth-order polynomial. Least-squares fitting of multiple Lorentzians and third-order polynomial background was

applied to the corrected data using a procedure based on the Minuit function minimization library. The fits to the background-corrected and raw data were visually compared in addition to obtaining an acceptable minimized χ^2 value for the least-squares fit. The resonances width and amplitude were strongly correlated with the background.

TF- μ SR measurements on 8hq at 298 K were performed using the HELIOS spectrometer in a magnetic field of 1.45 T. TF- μ SR measurements of Alq₃ at 298 K were performed on the HELIOS spectrometer in a magnetic field of 1.45 T. TF- μ SR measurements of Alq₃ at 10 and 298 K were performed on the HAL-9500 spectrometer at Swiss Muon Source (Paul Scherrer Institute, Villigen, Switzerland) in magnetic fields of 0.25 and 3.0 T.

DFT calculations were performed using the Gaussian 09 package of programs. The structures were optimized using the unrestricted B3LYP functional and the 6-311+G(d,p) basis set. Muonium was treated as an isotope of hydrogen with a magnetic moment of 8.890 597 μ_N . The light mass of the muon was treated in a manner suggested by Roduner.²⁸ The structure was first optimized with no constraints. The structure was then reoptimized with the bond corresponding to the C–Mu bond constrained at a length 4.9% longer than the optimized value.

ALC- μ SR spectra were simulated using the program Quantum.²⁰ Only the Δ_1 and methylene proton Δ_0 resonances were simulated for each radical.

III. RESULTS AND DISCUSSION

A. Benchmarking DFT calculations for related muoniated radicals

A criticism made about the DFT calculations in Ref. 17 was that the calculated hyperfine coupling constants did not match the values reported by Nuccio *et al.*²¹ This could be due to errors either in the calculations or in the previous μ SR measurements. The first step to resolving this controversy is to validate the DFT calculations by comparing the calculated values for several muoniated radicals with the experimentally measured muon and methylene proton hfccs. These are reported in Table I. There is very good agreement between the experimental and calculated values; the average magnitude of the % difference is 2.2% for A_μ and 3.4% for A_p . The results of the benchmarking calculations suggests that the computational method used in this paper is appropriate for the study of muoniated radicals formed by Mu addition to aromatic systems and containing heteroatoms.

B. DFT calculations of the Mu adducts of 8hq and simulated ALC- μ SR spectra

The ALC- μ SR spectra of the Mu adducts of 8hq can be modeled using the calculated muon and methylene proton hyperfine parameters listed in Table II and the [supplementary material](#). The overall ALC- μ SR spectrum depends on the relative yield of each of the

TABLE I. Benchmarking DFT calculations [UB3LYP/6-311+G(d,p)] on muoniated radicals by comparing the calculated muon and methylene proton hyperfine coupling constants with the corresponding experimental values. The numbering is based on the IUPAC nomenclature. The calculated hfccs were obtained by fixing the C–Mu bond to be 4.9% longer than the optimized value and partially optimizing all other parameters. Muonium was treated as an isotope of hydrogen with a magnetic moment of 8.890 597 μ_N .

Parent	Site	A_μ^{exp} (MHz)	A_μ^{calc} (MHz)	% diff.	A_p^{exp} (MHz)	A_p^{calc} (MHz)	% diff.
Benzene ^a	1	514.409	517.39	0.57	126.04	130.53	3.44
Furan ^b	2	378.8	377.59	−0.32	100.2	98.28	−1.95
	3	497.0	478.91 ^c	−3.78	130	125.69 ^c	−3.43
Pyridine ^d	2	526.8	533.68	1.29	125.6	131.03	4.15
	3	503.9	518.00	2.72	118.1	125.35	5.79
Naphthalene ^e	1	357.0	372.04	4.04
	2	436.5	438.20	0.39
Triphenylene ^f	1	409.67	412.04	0.57	101.2	104.96	3.58
	2	439.42	465.43	5.59	107.69	112.91	4.63
Fluoranthene ^g	1	347.35	348.35	0.29	88.13	90.96	3.11
	2	402.25	406.55	1.06	100.93	103.46	2.45
	3	263.87	277.47	4.90	68.81	71.43	3.67
	7	434.86	446.52	2.61	111.01	114.30	2.88
	8	348.95	360.43	3.18	91.50	92.98	1.59

^aExperimental values from Ref. 26.

^bExperimental values from Ref. 29.

^cBoltzmann average of two structures at 298 K assuming rapid interconversion.

^dExperimental muon hfcc from Ref. 30 and methylene proton hfcc from Ref. 31.

^eExperimental values from Ref. 32.

^fExperimental values from Ref. 15.

^gExperimental values from Ref. 33.

TABLE II. Calculated [UB3LYP/6-311+G(d,p)] muon hfccs and relative energies of the Mu adducts of 8-hydroxyquinoline. The calculated hfccs were obtained by fixing the C-Mu bond to be 4.9% longer than the optimized value and partially optimizing all other parameters. Muonium was treated as an isotope of hydrogen with a magnetic moment of $8.890\,597\,\mu_N$.

Radical	A_μ (MHz)	A_p (MHz)	$B_{res}^{\Delta_1}$ (T)	$B_{res}^{\Delta_0}$ (T)	ΔE (eV)
2	416.77	105.51	1.53	1.66	0.233
3	437.29	107.62	1.61	1.76	0.293
4	385.60	98.53	1.42	1.54	0.058
5	305.85	69.34	1.12	1.27	0.000
6	438.76	112.92	1.61	1.74	0.291
7	354.44	92.09	1.30	1.40	0.095

muoniated radicals and we have accounted for this by summing up the individual spectra multiplied by a factor representing the probability that it is formed. We considered two possibilities in simulating the overall ALC- μ SR spectrum. The first was that the relative yield of each type of muoniated radical depends on the rates that the radicals are formed. The amount of each type of radical that *could* form is the result of competition kinetics. The relative yield (P_{R_i}) of the muoniated radical R_i is given by

$$P_{R_i} = \frac{k_M^{R_i}[R_i]}{\sum_j k_M^{R_j}[R_j]}, \quad (3)$$

where k_M^j is the second-order rate constant for reaction j and $[R_j]$ is the concentration of the j th reaction partner. This can be the concentration of different molecules or different sites on the same molecule. This is observed for Mu addition in the liquid state.³³ Since we are considering different sites on the same molecule and each site is present in the same amount, Eq. (3) reduces to

$$P_{R_i} = \frac{k_M^{R_i}}{\sum_j k_M^{R_j}}. \quad (4)$$

The relative yield just depends on the rate constants for addition at the different sites. We will also assume that the rate constants can be described by the Arrhenius equation,

$$k_M^{R_j} = A e^{-\frac{E_{a,j}}{k_B T}}, \quad (5)$$

where $E_{a,j}$ is the activation energy, k_B is the Boltzmann constant, and T is the temperature.

According to the Bell-Evans-Polanyi hypothesis, the activation energy is linearly related to the reaction enthalpy (ΔH_j) for a series of related single-step reactions,³⁴

$$E_{a,j} = E_0 + \alpha \Delta H_j, \quad (6)$$

where α is a measure of “lateness” of the transition state ($0 > \alpha > 1$). This indicates that the activation energy is lower for more exothermic reactions (i.e., more negative ΔH). The corollary to this is the reaction is fastest for the pathways that generate the most stable free radical.

In order to simulate the overall spectrum, we have made several assumptions for addition of Mu at the different sites; (1) the pre-factor, A , is the same; (2) the “lateness” of the transition state, α ,

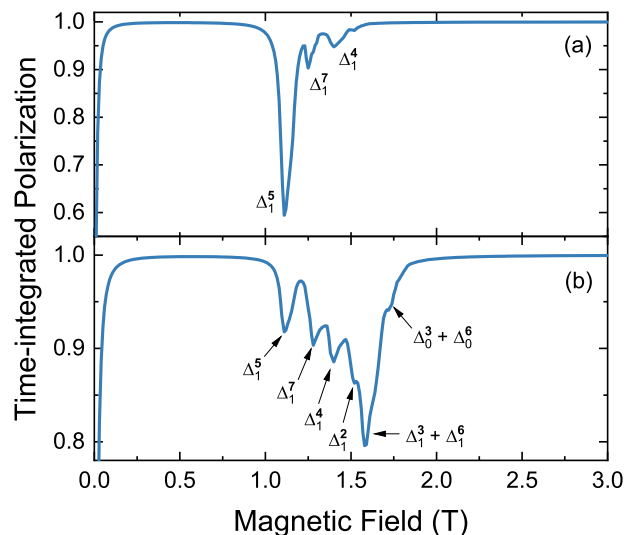


FIG. 5. Simulated ALC- μ SR spectra of 8hq powder with an electron spin flip rate of $1\,\mu\text{s}^{-1}$ (a) with the relative yield of each type of muoniated radical is given by the Boltzmann weighting with respect to the relative energy of the radical at 298 K (7) and (b) every muoniated radical formed in equal amount.

is the same; and (3) $\Delta H_i \sim \Delta H_0 + \Delta E_i$, where ΔH_0 is the reaction enthalpy for the most exothermic reaction and ΔE_i is the difference in the internal energy of the muoniated radical R_i and that of the lowest energy product. Combining the two previous equations and applying our assumptions gives

$$P_{R_i} = \frac{e^{-\Delta E_i/k_B T}}{\sum_j e^{-\Delta E_j/k_B T}}. \quad (7)$$

The relative yields, P_{R_i} , were used to produce the spectrum shown in Fig. 5(a). We also considered the possibility that the six types

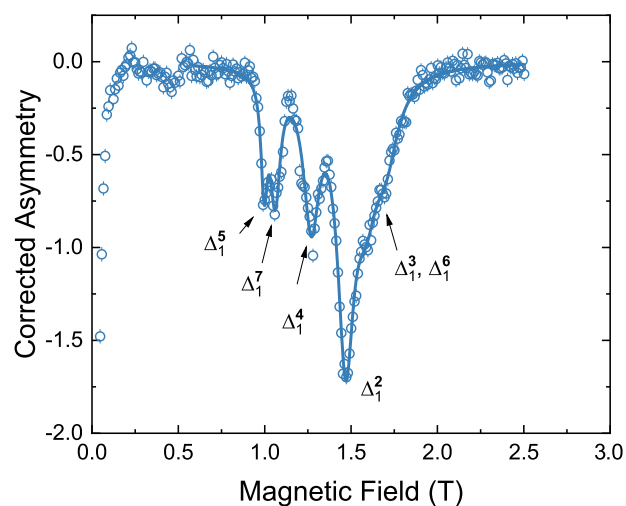


FIG. 6. Background-subtracted ALC- μ SR spectra of 8hq powder at 298 K.

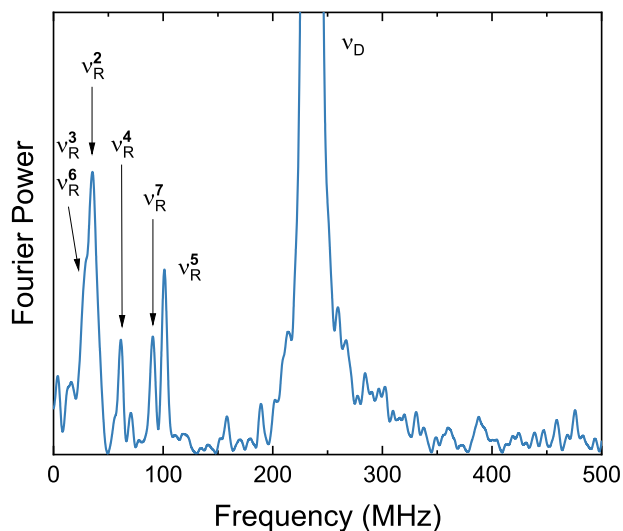


FIG. 7. TF- μ SR spectra of 8hq powder at 298 K with a Fourier transform window of 5 ns–0.7 μ s.

of muoniated cyclohexadienyl radical formed by addition to the secondary carbons of the aromatic ring were formed with equal probability, i.e., $P_{R_i} = 1/6$. The simulated ALC- μ SR spectrum for this scenario is shown in Fig. 5(b). In both cases, the amplitude of the Δ_0 resonances were negligible compared with the Δ_1 resonances.

C. μ SR measurements of 8hq

The ALC- μ SR and TF- μ SR spectra of 8hq powder at 298 K are shown in Figs. 6 and 7, respectively. There are four distinct

TABLE III. Muon hyperfine coupling constants of the Mu adducts of 8-hydroxyquinoline powder at 298 K determined by ALC- μ SR and TF- μ SR spectra.

Radical (s)	ALC- μ SR A_μ (MHz)	TF- μ SR A_μ (MHz)
5	271.6 ± 0.3	267 ± 2
7	288.9 ± 0.5	289 ± 2
4	345.8 ± 0.4	347 ± 2
2	400.0 ± 0.4	399 ± 2
3, 6	432 ± 2	410 ± 5

peaks in the ALC- μ SR spectrum with a shoulder to the highest field peak, suggesting additional unresolved resonances. The experimental spectrum greatly resembles the simulated spectrum where all of the radicals are formed in equal amounts. This could indicate that Mu is not thermalized prior to addition. There are also four radical frequencies in the TF- μ SR spectrum and the peak at ~ 40 MHz is considerably broader than the other radical lines, which could indicate unresolved signals. The resonances in the ALC- μ SR spectrum can be identified as Δ_1 resonances due to the resulting A_μ values matching those obtained from the radical lines in the TF- μ SR spectrum (Table III). The width of the resonances indicates that there is no significant electron hopping (Fig. 2).

The resonances were assigned by comparing the experimental ALC- μ SR spectrum with the simulated spectrum. The calculated hfccs are about 20% larger than the measured values, but there are clear similarities between the experimental spectrum and the simulated spectrum in which all possible radicals are formed with equal yield. Our assignment is based on the *pattern* of the resonances and a comparison with the DFT calculations. These are given in Table III and shown in Figs. 6 and 7. The smaller measured A_μ values could indicate a small amount of delocalization of the unpaired

TABLE IV. Calculated [UB3LYP/6-311+G(d,p)] muon hfccs and relative energies of the Mu adducts of Alq₃. The labeling of the muoniated radicals is based on the numbering scheme in 1 with the final number indicating different orientations of the muon with respect to the molecule. The calculated hfccs were obtained by fixing the C-Mu bond to be 4.9% longer than the optimized value and partially optimizing all other parameters. Muonium was treated as an isotope of hydrogen with a magnetic moment of 8.890 597 μ_N .

Position	A_μ (MHz)	ΔE (eV)	Position	A_μ (MHz)	ΔE (eV)	Position	A_μ (MHz)	ΔE (eV)
A2.1	320.80	0.146	B2.1	292.70	0.184	C2.1	358.70	0.166
A2.2	305.65		B2.2	361.27		C2.2	316.73	
A3.1	432.68	0.476	B3.1	455.02	0.471	C3.1	422.43	0.460
A3.2	435.02		B3.2	413.99		C3.2	444.67	
A4.1	292.45	0.053	B4.1	304.01	0.064	C4.1	314.52	0.075
A4.2	288.78		B4.2	291.90		C4.2	306.29	
A5.1	210.71	0.009	B5.1	212.50	0.016	C5.1	223.74	0.029
A5.2	204.92		B5.2	213.01		C5.2	227.09	
A6.1	446.77	0.458	B6.1	449.89	0.450	C6.1	445.69	0.449
A6.2	445.80		B6.2	438.83		C6.2	435.86	
A7.1	252.14	0.000	B7.1	252.02	0.022	C7.1	272.63	0.049
A7.2	251.52		B7.2	261.43		C7.2	258.38	

TABLE V. Calculated Δ_1 resonance field ranges of the Mu adducts of Alq_3 determined using the hyperfine parameters in Table IV.

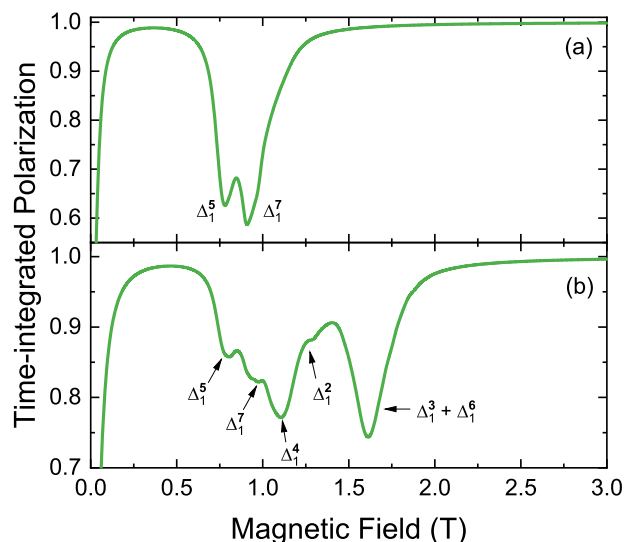
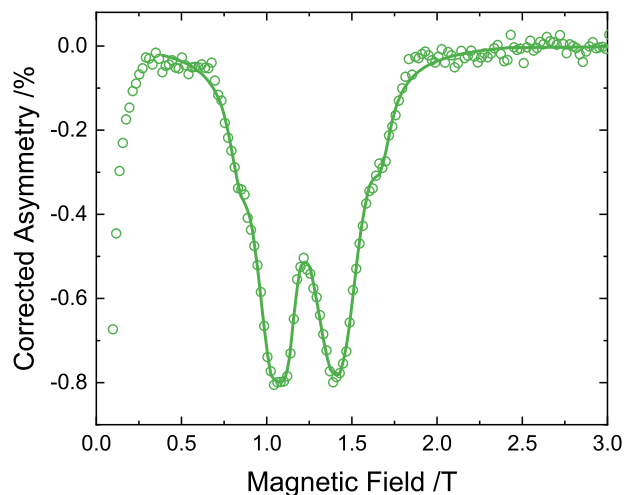
Radical (s)	Δ_1 (T)
5	0.739–0.804
7	0.935–0.999
4	1.039–1.124
2	1.075–1.326
3	1.469–1.620
6	1.585–1.631

spin density onto neighboring molecules but are more likely due to small changes in the structure due to interactions with neighboring molecules in the solid state.

D. DFT calculations of the Mu adducts of Alq_3 and simulated ALC- μ SR spectra

The calculated A_μ values and relative energies of the Mu adducts of Alq_3 are listed in Table IV. The calculated Δ_1 resonance field ranges are listed in Table V. There exist much larger differences between the A_μ values of diastereomers in this case than there are in the muoniated cyclohexadienyl radicals formed by Mu addition to l-phenyl-ethylamine, 1-phenyl-ethanol, and cumene.¹⁶

Spectra were simulated for each of the 36 muoniated radicals listed in Table IV using the isotropic and dipolar muon and methylene proton hfccs (supplementary material). Spectra were simulated first by assuming the relative yield of each type of radical is given by a Boltzmann average of the calculated relative energies [Eq. (7)] and then by assuming each radical is formed with equal yield (Fig. 8).

**FIG. 8.** Simulated ALC- μ SR spectra of Alq_3 powder with an electron spin flip rate of $20 \mu\text{s}^{-1}$ (a) with the relative yield of each type of muoniated radical given by Boltzmann weighting with respect to the relative energy of the radical at 298 K (7) and (b) every muoniated radical formed in equal amount.**FIG. 9.** Background-subtracted ALC- μ SR spectra of Alq_3 powder at 298 K.

E. μ SR measurements of Alq_3

The background-subtracted ALC- μ SR spectrum of Alq_3 at 298 K is shown in Fig. 9. There are several overlapping resonances that are assumed to be Δ_1 resonances based on their amplitude. There are two major resonances at ~ 1.08 and 1.41 T with shoulders at ~ 0.85 and 1.62 T. The major resonances correspond to A_μ values of ~ 294 and 384 MHz. The shoulders correspond to A_μ values of ~ 232 and 441 MHz. As with 8hq, the ALC- μ SR spectrum of Alq_3 most resembles the simulated spectrum where the radicals are formed with equal yield. The situation where the muoniated radicals are formed with a relative yield depending on their relative energy results in a spectrum where the resonances are at much lower fields than observed experimentally. We have not assigned the peaks in the ALC- μ SR spectrum of Alq_3 to individual muoniated radicals as the overlap makes this impractical.

TF- μ SR spectra of Alq_3 at 298 and 10 K are shown in Fig. 10. Fourier transforming over short time windows makes it possible to detect signals due to short-lived muoniated radicals. There are overlapping powder spectra of several muoniated radicals with muon hfccs on the order of 250–450 MHz. This is consistent with the ALC- μ SR spectra.

Drew *et al.* reported two types of muoniated radical with $|A_\mu|$ of 23 ± 1 and 91 ± 1 MHz at 10 K and not, as implied, at 290 K.⁹ We found no evidence for muoniated radicals with hfccs in this range in the TF- μ SR spectrum of Alq_3 at either 10 or 298 K. This was true for the TF- μ SR measurements on HAL-9500 at 3.0 and 0.25 T and HELIOS at 1.45 T (supplementary material).

The simulated resonances in the ALC- μ SR spectrum are comparable in width to the experimental resonances when including an electron spin flip rate of tens of μs^{-1} (Fig. 2). We suggest that this means that there are dynamic processes that lead to the relaxation of the muon spin in the OSC and this does not occur in 8hq. Grecu *et al.* performed EPR measurements on non-doped Alq_3 and found several paramagnetic defect centers corresponding to $1/2$, 1, and $3/2$ spin at room temperature.³⁶ It is possible that the Mu adducts of Alq_3 interact with these paramagnetic states, particularly the state

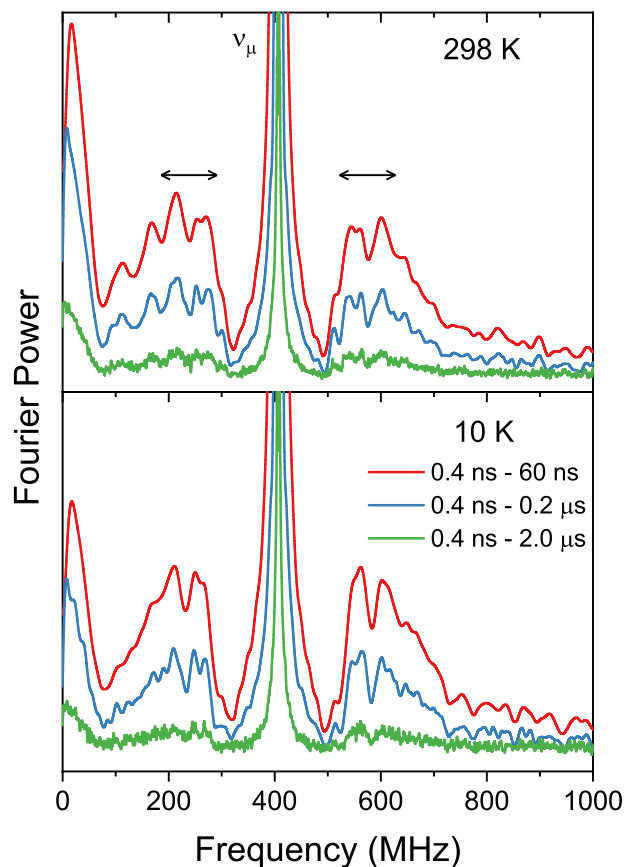


FIG. 10. TF- μ SR spectra of Alq₃ powder at 298 K (top) and 10 K (bottom) in a magnetic field of 3.0 T with different time windows for the Fourier transformation (ftw3 as implemented in musrfit³⁵). The horizontal lines denote the range of frequencies corresponding to the muon hyperfine couplings determined from the ALC- μ SR measurement.

assumed to be the radical anion where the unpaired electron is mobile, which could cause spin relaxation by the Heisenberg spin-exchange reaction. The rate for this process is on the order of tens of μs^{-1} , which is approximately five orders of magnitude slower than that suggested by Drew *et al.*

IV. CONCLUSIONS

The magnitude of the A_μ values of the Mu adducts of 8hq and Alq₃ clearly shows that the unpaired electron spin density is localized on the same Alq₃ molecule to which Mu is covalently bound. No muoniated radicals with $|A_\mu|$ in the range of 23 ± 1 and 91 ± 1 MHz were observed in the TF- μ SR spectrum. The observed muoniated radicals have substantially different energy levels compared with the parent molecules and this results in the unpaired electron being pinned. This indicates that μ SR cannot be used to measure the intrinsic hop rate of electrons in Alq₃. ALC resonances were observed in TIPS-pentacene³⁷ and other organic semiconductors based on polyaromatic hydrocarbons, so it is likely that a similar pinning of the charge is occurring in these systems as well, but further

investigation is required. This is not to say that μ SR studies of the Mu adducts of Alq₃ and other OSC could not provide information about organic semiconductors. The resonance widths are broader than expected in Alq₃ and this could be due to interactions between the muoniated radicals and other paramagnetic species in the OSC. Further measurements are needed to see if the broadening is related to the concentration of defects in Alq₃.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for calculated muon and methylene proton isotropic and dipolar hyperfine coupling constants of 8-hydroxyquinoline and Alq₃ and for additional TF- μ SR spectra of Alq₃.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Iain McKenzie: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Project administration (lead); Writing – original draft (equal); Writing – review & editing (equal). **Joseph Cannon:** Formal analysis (supporting); Investigation (supporting). **Danaan Cordoni-Jordan:** Formal analysis (supporting); Investigation (supporting). **Brian P. Mulley:** Formal analysis (supporting); Investigation (supporting). **Robert Scheuermann:** Conceptualization (equal); Formal analysis (equal); Investigation (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

Raw data were generated at the TRIUMF and Paul Scherrer Institute large scale facilities. Derived data supporting the findings of this study are available from the corresponding author upon reasonable request.

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