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Transverse spin relaxation time in organic molecules

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We report a measurement of the ensemble-averaged transverse spin relaxation time (T_2^*) in bulk and few molecules of the organic semiconductor *tris-(8-hydroxyquinolinolato aluminum)* or Alq$_3$. This system exhibits two characteristic T_2^* times: the longer of which is temperature independent and the shorter is temperature dependent, indicating that the latter is most likely limited by spin-phonon interaction. Based on the measured data, we infer that the single-particle T_2 time is probably long enough to meet Knill's criterion for fault-tolerant quantum computing even at *room temperature*. Alq$_3$ is also an optically active organic, and we propose a simple optical scheme for spin qubit readout. Moreover, we found that the temperature-dependent T_2^* time is considerably shorter in bulk Alq$_3$ powder than in few molecules confined in 1–2-nm-sized cavities. Because carriers in organic molecules are localized over individual molecules or atoms but the phonons are delocalized, we believe that this feature is caused by phonon bottleneck effect.

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The π-conjugated organic semiconductor Alq$_3$ exhibits exceptionally long longitudinal spin relaxation time T_1 (approaching 1 s at 100 K) because of weak spin-orbit interactions.[1] That bodes well for classical-spin-based devices such as spin enhanced organic light emitting diodes[2] or *classical*-spin-based computing paradigms, such as single spin logic[3,4] where a long T_1 time reduces the probability of bit errors caused by unwanted spin flips. In *quantum* computing paradigms,[5–10] the bit error probability depends on the transverse spin relaxation time T_2 rather than T_1. The probability of a spin-based qubit to decohere during a qubit operation that lasts for a time duration T is roughly $1-e^{-T/T_2}$. Knill[11] showed that fault-tolerant quantum computing becomes possible if this probability is less than 3%, i.e., if $T_2/T > 33$.

Two recent results have inspired us to look toward the Alq$_3$ molecule as a potential candidate for fault-tolerant spin-based quantum computing. The first is the demonstration that it exhibits a long T_1 time.[1] This results from weak spin-orbit interactions which could also make the T_2 time long enough to allow fault-tolerant computing. Second, some organic molecules can be efficient quantum processors with high gate fidelity.[12] These two factors, taken together, raise the hope that Alq$_3$ might be a preferred platform for spin-based quantum computing. This molecule also has spin-sensitive optical transitions that can be gainfully employed for spin (qubit) readout. That makes it even more attractive.

Unfortunately, it is very difficult to measure the single-particle T_2 time directly in any system (including Alq$_3$ molecules) since it requires complicated spin-echo sequences. Therefore, we have measured the ensemble-averaged T_2^* time instead since it can be ascertained easily from the linewidth of electron-spin-resonance (ESR) spectrum. This time, however, is orders of magnitude shorter than the actual T_2 time of an isolated spin because of additional decoherence caused by interactions between multiple spins in an ensemble.[13,14] It is particularly true of organics where spin-spin interaction is considered to be the major mechanism for spin decoherence.[15] Consequently, bulk samples (where numerous spins interact with each other) should behave differently from samples consisting of one or few molecules containing fewer interacting spins. In the rest of this Brief Report, we will designate the T_2^* times of bulk- and few-molecule samples as T_2^b and T_2^f, respectively. We have found that they are discernibly different.

In order to prepare samples containing one or few molecules, we followed the approach in Ref. 16. We first produced a porous alumina film with 10 nm pores by anodizing an aluminum foil in 15% sulfuric acid.[17] A two-step anodizing process was employed to improve the regimentation of the pores.[18] These porous films were then soaked in 1, 2-dichloroethane ($C_2H_4Cl_2$) solution of Alq$_3$ for over 24 h to impregnate the pores with Alq$_3$ molecules. The films were subsequently washed several times in pure $C_2H_4Cl_2$ to remove excess Alq$_3$. There are cracks of size 1–2 nm in the anodic alumina film produced in sulfuric acid.[16,19,20] Reference 16 claimed that when the anodic alumina film is soaked in Alq$_3$ solution, Alq$_3$ molecules of 0.8 nm size diffuse into the cracks and come to rest in nanovoids nestled within the cracks. Since the cracks are 1–2 nm wide, only one to two molecules of Alq$_3$ can reside in the nanovoids. Surplus molecules, not in the nanovoids, will be removed by repeated rinsing in $C_2H_4Cl_2$.[16] $C_2H_4Cl_2$ completely dissolves out all the Alq$_3$ molecules, except those in the nanovoids, because the $C_2H_4Cl_2$ molecule cannot easily diffuse through the 1–2-nm-wide nanocracks to reach the nanovoids (Fig. 1). Therefore, after the repeated rinsing procedure is complete, we are left with an ensemble of few-molecule clusters in the nanovoids. The nanovoids are sufficiently far from each other that interaction between them is negligible.[16] Therefore, if we use the fabrication technique of Ref. 16, we will be confining one or two isolated molecules in nanovoids and measuring their T_2^f times. In contrast, the T_2^b times are measured in bulk Alq$_3$ powder containing a very large number of interacting molecules.

The T_2^f and T_2^b times were measured using ESR spectros-

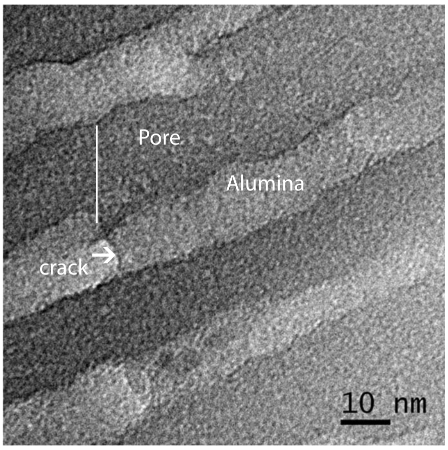

FIG. 1. Cross-section transmission electron micrograph of porous alumina film containing 10-nm-diameter pores. A nanocrack of diameter 1–2 nm is shown.

copy. In each run, 20 samples of area 25 mm^2 each were stacked. They together contain 5×10^{11} pores, and even if each pore contains at least one molecule and each molecule contains at least one electron (extremely conservative estimate), we still have over 5×10^{11} electrons, which are more than adequate to provide a strong spin signal (our equipment can measure signals from 1×10^{9} spins).

It is well known that Alq_3 has two spin resonances corresponding to Landé g factors of approximately 2 and 4.[21] Reference 21 determined from the temperature dependence of the ESR intensity that the $g=4$ resonance is associated with localized spins in Alq_3 (perhaps attached to an impurity or defect site) while the $g=2$ resonance is associated with quasifree (delocalized) spins. From the measured linewidths of these two resonances, we can estimate the T_2^f and T_2^b times for each resonance individually using the standard formula

$$T_2^f \text{ or } T_2^b = \frac{1}{r_e(g/2)\sqrt{3}\Delta B_{pp}}, \qquad (1)$$

where r_e is a constant that is equal to $1.76\times 10^{7}(\text{G}-\text{s})^{-1}$, g is the Landé g factor, and ΔB_{pp} is the full width at half maximum of the ESR line shape (the "linewidth"). We checked that the line shape is almost strictly Lorentzian, so that the above formula can be applied with confidence.[22] Figure 2 shows a typical magnetic-field derivative of the ESR spectrum obtained at a temperature of 10 K corresponding to $g=2$ resonance. There are three curves in this figure corresponding to the blank alumina host, bulk Alq_3 powder, and Alq_3 in 1–2 nm voids. The alumina host has an ESR peak at $g=2$ (possibly due to oxygen vacancies),[23] but it is much weaker than the resonance signals from Alq_3 and hence can be easily separated. Note that the g factor of the isolated Alq_3 molecules in nanovoids is slightly larger than that of bulk powder since the resonance occurs at a slightly higher magnetic field. More importantly, the bulk powder has a broader linewidth than the few molecules confined in the nanovoids. This is a manifestation of the fact that stronger spin-spin interactions in the bulk powder reduce the effective T_2^* time, i.e., $T_2^b < T_2^f$.

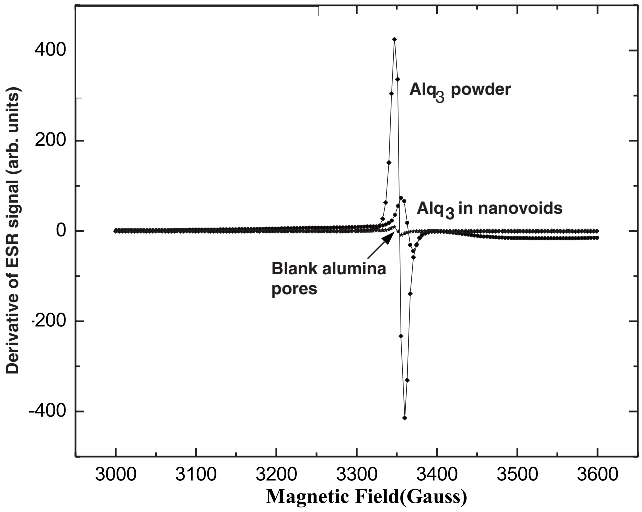

FIG. 2. First derivative in magnetic field of the electron-spin-resonance spectrum corresponding to $g=2$. The three curves are the data for the blank alumina matrix, the Alq_3 powder, and Alq_3 molecules in nanovoids. The temperature is 10 K.

In Fig. 3, we plot the measured T_2^f and T_2^b times (associated with the resonance corresponding to $g=2$) as functions of temperature from 4.2 to 300 K. The inequality $T_2^b < T_2^f$ is always satisfied except at one anomalous data point at 4.2 K. There are two important points to note here. First, both T_2^f and T_2^b are relatively temperature independent over the entire range from 4.2 to 300 K. This indicates that spin-phonon interactions do not play a significant role in spin dephasing. Second, both T_2^f and T_2^b times are quite long, longer than 3 ns, even at room temperature.

In Fig. 4, we plot the measured T_2^f and T_2^b times as functions of temperature corresponding to the $g=4$ resonance. The T_2^f time is plotted from 4.2 to 300 K, but the T_2^b time in bulk powder can only be plotted up to a temperature of 100 K. Beyond that, the intensity of the ESR signal fades below

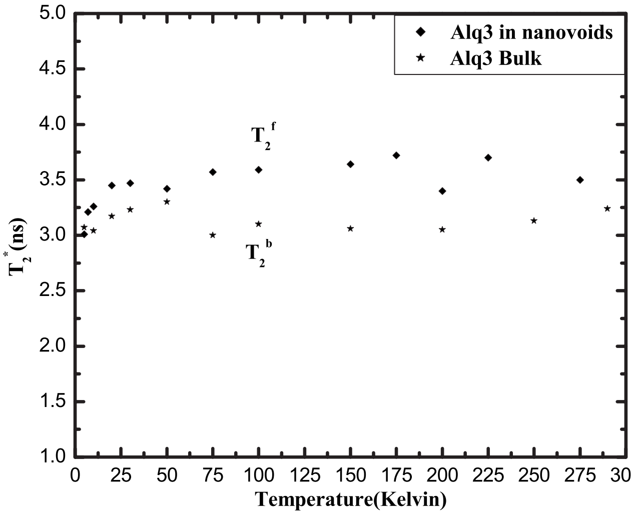

FIG. 3. Transverse spin relaxation times as a function of temperature for $g=2$ resonance. The two plots are for bulk Alq_3 powder (T_2^b) and few Alq_3 molecules in nanovoids (T_2^f).

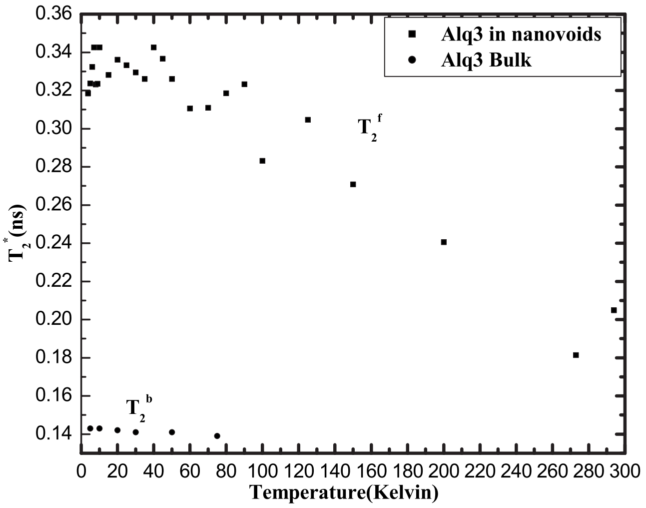

FIG. 4. Transverse spin relaxation times as a function of temperature for $g=4$ resonance. The two plots are for bulk Alq_3 powder (T_2^b) and few Alq_3 molecules in nanovoids (T_2^f).

the detection limit of our equipment. The features to note here are: (1) T_2^f and T_2^b are no longer temperature independent unlike in the case of the $g=2$ resonance, and T_2^f decreases monotonically with increasing temperature and falls by a factor of 1.7 between 4.2 and 300 K; (2) $T_2^b < T_2^f$ and the ratio T_2^f/T_2^b decreases with increasing temperature, and the maximum value of the ratio T_2^f/T_2^b is 2.4, occurring at the lowest measurement temperature of 4.2 K; and (3) both T_2^f and T_2^b times are about an order of magnitude shorter for the $g=4$ resonance compared to the $g=2$ resonance.

The strong temperature dependence of T_2^f and T_2^b tells us that for $g=4$ resonance, spin-phonon coupling plays the dominant role in spin dephasing instead of spin-spin interaction. The spin-phonon coupling is absent or significantly suppressed for the $g=2$ resonance, which is why T_2^f and T_2^b are an order of magnitude longer and also temperature independent for $g=2$. Reference 21 has ascribed the $g=2$ resonance to quasi-free-carrier spins in Alq_3 (whose wave functions are extended over an entire molecule) and $g=4$ resonance to localized spins (whose wave functions are localized over an impurity atom). If that is the case, then it is likely that the localized spins and the delocalized spins will have very different couplings to phonons since their wave functions are very different.

An interesting question is why should T_2^f be so much longer than T_2^b for the $g=4$ resonance. The bulk has many more interacting spins than the few-molecule sample has, but if spin-spin interaction is overshadowed by spin-phonon coupling, then this should not make any difference. Therefore we believe that what causes this behavior is a "phonon-bottleneck effect." For $g=4$ resonance, we know that the primary dephasing agents are phonons. So what makes the spin-phonon coupling so much stronger in bulk than in nanovoids? In bulk Alq_3 powder, the phonons are not confined and form a continuum. However, in isolated nanovoids (cavities) of ~2 nm diameter, the phonons are confined so that only discrete phonon modes are allowed. Any dephasing transition will then have to emit or absorb a subset of these allowed phonon modes. This reduces the transition probability considerably since few phonons are available to satisfy the energy and momentum conservations for phonon emission and absorption. This is another type of phonon-bottleneck effect, slightly different from the one discussed in Ref. 24, which required carrier confinement more than phonon confinement. This different type of phonon-bottleneck effect would explain why $T_2^f > T_2^b$ when phonons are the primary dephasing agents. The bottleneck will be more severe at lower temperatures since fewer phonon modes will be occupied (Bose-Einstein statistics), which is exactly what we observed. If this explanation is true, it will be, to our knowledge, the first observation of this effect in organic molecules. What makes it more intriguing is the fact that there is no "quantum confinement" effect on electrons since their wave function is at best extended over a single molecule which is only ~0.8 nm in size, but the phonon modes are extended over many molecules, and therefore, do suffer quantum confinement if the confining space is a nanovoid of ~2 nm in diameter. We raise the specter of phonon bottleneck only as a possibility but cannot confirm it experimentally beyond all reasonable doubt since that would require showing progressive suppression of dephasing with decreasing nanovoid size, something that is experimentally not accessible. Nonetheless, we believe that there is a strong suggestion for the phonon-bottleneck effect.

We conclude by discussing the suitability of Alq_3 molecules for quantum computing applications. For a single isolated spin in Alq_3, T_2 should be at least an order of magnitude longer than T_2^* (Refs. 13 and 14) particularly when spin-spin interaction is the major dephasing mechanism ($g=2$). Since we have measured that $T_2^* \sim 3$ ns at nearly all temperatures between 4.2 and 300 K for $g=2$ resonance, we expect that the single spin T_2 time will be at least 30 ns over this entire temperature range. Now, if Rabi oscillation is used for qubit operations such as rotation,[7,8] then the time taken to effect a complete spin flip is $T=h/(2g\mu_B B_{ac})$ where g is the Landé g factor, μ_B is the Bohr magneton, and B_{ac} is the amplitude of the ac magnetic field inducing the Rabi oscillation. With $B_{ac}=500$ G,[25] $T=0.35$ ns. Therefore, the error probability is equal to $1-\exp[-T/T_2]=1.15\%$. This is *less* than the Knill limit of 3% for fault-tolerant quantum computing, which is encouraging. We emphasize that Alq_3 does not have exceptionally long T_2 times, but it is still adequate for fault-tolerant quantum computing. Nitrogen vacancy (NV^-) in diamond exhibits a much longer T_2 time of several tens of microsecond at room temperature.[26] However, quantum computing paradigms based on NV^- require optical gating[27,28] or cavity dark states,[29] since it would be nearly impossible to place an electrical gate on top of an atomic vacancy using any of the known fabrication methods. As a result, NV^- computers are not truly scalable. In contrast, the spins in Alq_3 are not bound to specific atomic sites. Instead, they extend over molecules of size ~1 nm, which allows electrical gating and therefore scalable renditions of quantum processors. Inorganic semiconductor qubit hosts, that will also allow electrical gating, typically have a shorter T_2^* time than Alq_3 at room temperature.[30] Therefore, the Alq_3 system deserves due attention.

Finally, if an Alq_3 quantum dot was used as a host for a spin qubit, one would require a mechanism for reading the host spin (qubit readout). Fortunately, this can be achieved quite simply and elegantly. It is well known that only the singlet exciton recombines radiatively in Alq_3 and the triplet does not.[2] Thus, one needs to inject a spin polarized hole into an Alq_3 quantum dot that hosts a single electron in the lowest unoccupied molecular orbital (LUMO) level from a *p*-type dilute magnetic semiconductor such as GaMnAs. The hole spin will be known (majority spin in GaMnAs). If a photon is emitted from the Alq_3 quantum dot, then we will know that the electron and the hole spins are antiparallel. Otherwise, they are parallel. This allows one to determine the electron spin polarization in the Alq_3 dot (qubit readout). The optical readout mechanism requires a quantum dot photon detector to be integrated on top of the Alq_3 quantum dot hosting the spin. This is not difficult to implement[31] and does not detract from the scalability. In conclusion, Alq_3-based quantum processors (1) are scalable, (2) are capable of fault-tolerant operation at room temperature, (3) possibly have a high degree of gate fidelity, and (4) lend themselves to an elegant qubit readout scheme. This makes them attractive candidates for quantum computers.

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