Tune-ability and criticality in a 3D stacked molecular system

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With the changing of physical properties through chemical substitution in mind, this work shows the applicability of this approach to organic based spin-Peierls (SP) systems. To demonstrate this we have used a well known system, potassium TCNQ, that undergoes an SP transition at T_{SP} =396 K. Simply substituting protons for fluorine, using TCNQF$_4$, shows a decrease in the coupling strength between TCNQ anions where the spin-Peierls transition is dramatically reduced in temperature, with KTCNQF$_4$ showing a T_{SP} at approximately 160 K, which is due to changes of the electron spin density across the molecule. Muon spin relaxation is a more ideal technique for determining the magnetic properties of these systems and measurements were conducted on both KTCNQ and KTCNQF$_4$ in order to study the behaviour of the SP transition. This has highlighted and shown that both transitions exhibit the same behaviour and so are indeed similar however we have succeeded in being able to tune the transition. Estimates of the dynamic critical exponents from both samples are obtained from the muon data and are found to be ~ 0.33, corresponding to a 3D antiferromagnetic system implying that spin fluctuations associated with the SP state are correlated not just along stacks of dimerised TCNQ anions. This result extends the understanding of the SP phase transition in the KTCNQ system beyond that determined from purely structural studies.

One of the ultimate goals in the physical and chemical sciences is to create systems that can be tuned or made to do what we want, when we want. To this end, one of the most fruitful procedures for doing this is taking a compound/molecule that shows a particular property we are interested in, such as magnetism, and changing it in an attempt to cause shifts in physical properties. This is one argument for the application of pressure[1] in the search for new materials. However pressure can be applied in two ways, physical (or mechanical) or chemical[2,3]. The latter involves using chemical substitutions to cause shifts in the electronic structure of the molecule observable through its physical properties[4]. This is where organic based materials are of importance, the ease and simplicity in manipulating a molecule make this an exciting playing field for the creating of systems that show different physical properties but based on the same building blocks. This is ultimately achieved by subtle changes to the organic molecule, which can result in dramatic changes in the electronic structure and in turn change the magnetic and electronic properties[35,36]. This is no real surprise and for many is intuitive, especially when one considers the changes in electron distribution across simple diatomic molecules such as H-F *vs.* H-Cl where the F atom pulls electron density towards it due to the higher electro-negativity.

Our work focuses on utilising the molecule TCNQ (7,7,8,8-tetracyanoquinodimethane) that is a symmetric, planar molecule capable of forming a radical anion[18,19] and has a long history of being used to synthesise novel materials[20–22]. The radical electron density is delocalised across the entire molecule and one can therefore see that changing one substituent may have dramatic effects on the energy levels. Due to TCNQ's flat structure this makes it susceptible to π-stacking and forming 1D chains of the anion coupled through the π-orbitals in one direction. Indeed, due to this, TCNQ forms spin-Peierls systems, where there are strong structural and magnetic correlations between adjacent molecules (see Figure 1). The spin-Peierls (SP) state has had much interest throughout physics[5–8] as a 1D magnetic chain. and includes many charge transfer (CT) compounds[9,10] where, by altering the anion in such a CT salt, the properties can be changed, showing the fragility of the SP system to structural change[11]. In fact, within these type of CT materials where the electron is delocalised across a dimer, strong magneto-electric coupling has been observed where the samples show multiferroic behaviour[30,31]. An extensive study has also been conducted on CuGeO$_3$, a famous inorganic SP material[12–14] that shows well documented 3D ordering associated with T_{SP}[15], as do other examples such as TiPO$_4$[16] and NaV$_2$O$_5$[17].

Work presented in this manuscript focuses on potassium TCNQ[23,24] where there is a stacking of TCNQ anions along the a-axis and, below T_{SP}, there are alternating TCNQ-TCNQ distances due to the spin pairing mechanism[25]; an estimate of the exchange energy between the magnetically coupled dimers is $J' = -1800$ K[8]. Firstly, we show that the TCNQ-TCNQ interactions along the stacks can be altered by simple substitution of protons on the TCNQ aromatic ring using TCNQF$_4$ as the organic acceptor, due to changes in the spin density across the molecule. Magnetisation and muon spectroscopy measurements are used to study the magnetic behaviour (since T_{SP} is different between the susceptibility and muon spectroscopy we have used the notation T^{χ}_{SP} and T^{μ}_{SP} to avoid confusion). The muon spectroscopy has distinct advantages as it pro-

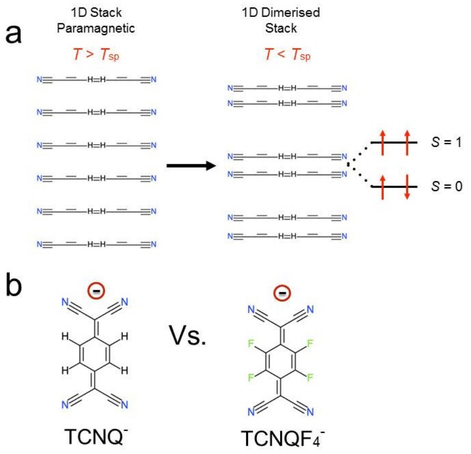

FIG. 1. **a.** Schematic representation of the spin-Peierls transition within KTCNQ. **b.** Molecular structure of the two TCNQ compounds used within this study. Below T_{SP} the 1D stacks of TCNQ anions are strongly correlated and dimers for where the ground state is a singlet. The negative charge or unpaired electron is delocalised across the entire molecules however most of the electron density resides at one end by two of the cyano groups (as shown in part **b**). Changing the aromatic substituents to will alter the probability distribution of the electron that gives rise to the magnetic moment of the molecule, where in the case of F and due to its increased electronegativity will pull electron density towards the ring away from the CN groups.

vides both a method to measure in zero-field, where application of a magnetic field causes broadening or distortion of transitions and also offers sensitivity to only para/ferromagnetism so that the diamagnetism may be neglected. The results show the universality of the SP transition and the muon relaxation in both the KTCNQ and KTCNQF$_4$ is dominated by strong magnetic fluctuations where, below T^{μ}_{SP}, a quasi-static magnetic state is observed on the time scale of the muon decay. Energies can be calculated for the spin gaps associated with the SP state as well as the dynamic exponent, which shows that one cannot simply think of this class of materials as a 1D chain of magnetic anions.

KTCNQ was synthesised by refluxing potassium iodide (99.99%) and TCNQ (>98%) in dry acetonitrile[18,19]. TCNQF$_4$ (>98%)[37]. For information on the powder diffraction data see the supplementary information. Magnetisation data was taken on a Quantum Design MPMS that has a maximum applied field of 7 T. Muon spectroscopy data were collected at the ISIS neutron and muon spallation source in the United Kingdom on the EMU spectrometer. Fitting of the raw μSR data was done using the WIMDA program[39].

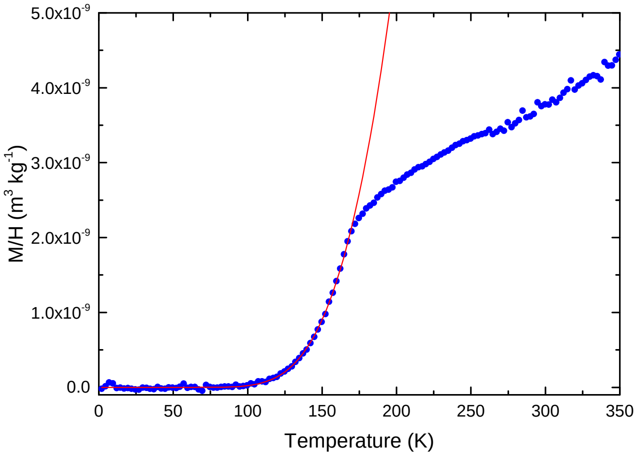

FIG. 2. M/H *vs.* T for KTCNQF$_4$ cooled in an applied field of 5 T where diamagnetic and low temperature Curie-Weiss contributions have been subtracted, the red line shows a fit to the data to estimate the energy associated with the spin gap. No sharp kink at T_{SP} is observed and is likely to be due to the high fields applied.

The magnetic data for KTCNQF$_4$ is shown in figure 2 where the data set below the transition temperature could be fitted using the equation

$$\chi = A_{SP} \exp\left(\frac{2\Delta}{k_B T}\right), \tag{1}$$

which was used previously to model the spin gaps within NaTiSi$_2$O$_6$ and TiOCl[40]. The paramagnetic and diamagnetic components were subtracted (see supplementary information) from the data to provide a clear illustration of the spin-Peierls transition as shown in figure 2. The value of $2\Delta/k_B = 1107(11)$ K, obtained from the fit using equation 1, gives the magnitude of the spin gap to be $\Delta \approx 554$ K, which is a huge reduction when compared with that of the protio sample, KTCNQ. Unfortunately, due to limitations of the equipment it was not possible to get magnetic data on the KTCNQ sample as this would require temperatures in excess of 350 K, which is not easily achievable on the MPMS. However, the magnetic properties of the salt are well documented elsewhere[26], which have been analysed and can be seen in the supplementary information. Using the same model as for the KTCNQF$_4$ sample, a value of $\Delta = 1639(71)$ K was calculated using the data collected by the Faraday method. Thus it is clear both samples have extremely different energy gaps associated with the SP state.

Since the magnetisation measurements present some problems, such as removing the paramagnetic impurity, diamagnetic components and potential complications of transitions within high fields, another technique is needed, namely, μSR. This presents significant advantages as the muon relaxation is sensitive to both spin dynamics and static ordering plus there is no contribution from the diamagnetic susceptibility nor should the low temperature paramagnetic Curie tail present an issue and the data are collected in zero-field so one can

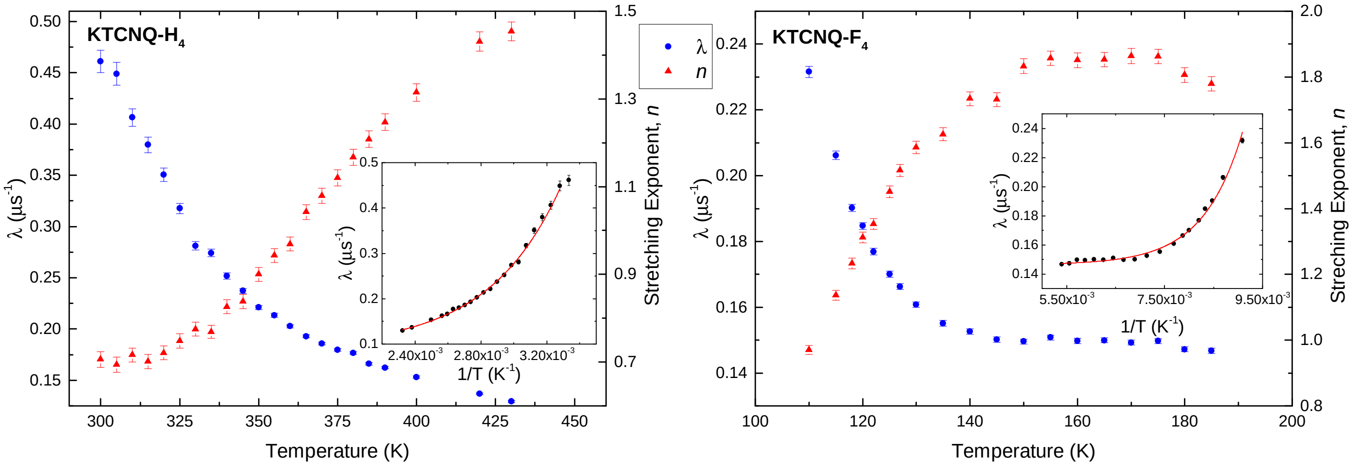

FIG. 3. Zero field μSR parameters; λ (blue circles) and the stretching exponent (red triangles) for KTCNQ-H$_4$ and KTCNQ-F$_4$ where T_{SP} has been defined as 324 and 100 K respectively .*Insets:* Plots of the muon relaxation *vs.* $1/T$ with fits to an activated behaviour (red line).

study the transition more accurately. Within this work experiments were conducted on both KTCNQ-H$_4$ and KTCNQ-F$_4$ in order to study the SP transition in zero field. Previous work[32,33] on MEM(TCNQ)$_2$ has shown that the stretching exponent parameter, n, shows an increase from approximately 1 to 2 on warming through T^{μ}_{SP}, the exponential character of the relaxation is due to fast electronic fluctuations which move outside of the muon time scale at high T where nuclear fields dominate the muon spin relaxation. It should be noted that one cannot assume the 1:2 and 1:1 salts are similar, there are fundamental differences between the chemical and physical properties within the systems that make them only comparable at face value. One should consider KTCNQ and the 1:1 salts more similar to the inorganic salts such as CuGeO$_3$.

Throughout the temperature range the raw μSR data (see supplementary information) could be fit using a stretched exponential function of the form

$$G(t) = A \cdot \exp(-(\lambda t)^n) + A_0, \tag{2}$$

similar to MEM(TCNQ)$_2$, where A is the relaxing asymmetry, λ is the muon relaxation rate, n is the stretching exponent and A_0 is the baseline or non-relaxing muons. The parameters from the fits can be seen in Figure 3 where in both cases it is clear that the muon relaxation rate is sensitive to the SP transition and the closing of the spin gap is observed as a drop in relaxation and increase in the stretching exponent. The increase in λ on going through T^{μ}_{SP} is due to the muon relaxation being dominated by magnetic fluctuations which freeze out as the sample enters a quasi-static state. At high temperature, the fluctuations are outside the experimental time scale and so the sample is in the motionally narrowed state. However, as T decreases and the fluctuations enter the muon time scale and the muon response is no longer motionally narrowed, but is still within the fast-fluctuating limit. This may present a problem when considering the relaxation and it's relation to dynamics, however this is beyond the context of this manuscript.

The T^{μ}_{SP} can be defined from the steepest part of the slope of λ *vs.* T which is approximately 320 K for KTCNQ-H$_4$ and between 90 and 110 K for the KTCNQ-F$_4$ sample. For more information on the justification of T^{μ}_{SP} please see the supplementary information. Within a system where there are fast fluctuations, the muon polarisation, $G(t) \propto \exp(-2\Delta^2_{fd} \cdot t/\nu)$, where Δ_{fd} is the width of random fields (in MHz) and ν is the fluctuation rate. In both cases, the results presented show the muon relaxation is dominated by fluctuations which are present to well below T^{χ}_{SP} calculated from the magnetic susceptibility where, at low T, the sample enters a quasi-static state on the time scale of the muon. At temperatures well below T^{μ}_{SP} the relaxation cannot accurately be modelled with a single exponential showing the complexity of the ground state where there is likely to be various muon-TCNQ interactions and thus a variety of field distributions as well as fluctuations still being present. Indeed above the transition, the fact that n does not tend to 2, which would indicate a static fields from magnetic order from nuclear moments, shows that there may be multiple muon stopping sites or the sample is not entirely in the motionally narrowed state so the muon is always sensitive to both a static nuclear field and an electronic magnetic fluctuation on the experimental time scale[45]. The asymmetry (not shown here) increases by 3% on going through the transition from 300 to 400 K, which is likely due to the strong coupling of the muon to the dimerised state of the TCNQ. At temperatures below the transition the relaxation is more complex but it is likely it is a result of the unfreezing of the quasi-static state as T is increased towards T^{μ}_{SP} (see supplementary information). The change in relaxing asymmetry for the KTCNQ-F_4 samples shows a small increase in 19.4 to 20.4% on going through the transition which is different to the protio sample, however it shows that the majority of muons are dephased within the experimental time scale. It should be noted that the baseline within this experiment differed at 2.5% from the protio sample.

The muon spin depolarization can be used to gain an indication of the SP energy gap and thus interaction strength of both systems in the temperature range studied by fitting the data with

$$\lambda = \lambda_{sp} \cdot \exp\left(\frac{E_a}{T}\right) + \lambda_0, \tag{3}$$

where λ_{sp} is the amplitude, E_a is the activation energy and λ_0 is the baseline, which in this case is a value for the field distribution of the muon relaxation from dipolar interactions with nuclear fields. The parameters extracted from the fits for KTCNQ-H_4 are $E_a = 2269(102)$ K, $\lambda_{SP} = 2.1(7)\times10^{-4}$ μs^{-1} and $\lambda_0 = 0.091(4)$ μs^{-1}. For KTCNQ-F_4 $E_a = 1242(65)$ K, $\lambda_{SP} = 1.1(6)\times10^{-6}$ μs^{-1} and $\lambda_0 = 0.146(1)$ μs^{-1}. If we make the same assumption as for the magnetic susceptibility and divide the activation energy by 2, resulting in a value of Δ, we arrive at values of 1135 K and 621 K for the protio and fluoro samples respectively. The value for the KTCNQF_4 is similar to that obtained from the magnetic susceptibility but for the KTCNQ sample, there is a discrepancy between the Δ values from the magnetic susceptibility and μSR data. Although there is a difference the trend still fits and it may simply be due to differences between the two measurement techniques. However, the muons and susceptibility do appear to be sensitive to the same phenomena, where the SP transition is strongly dominated by the slowing down of magnetic fluctuations. It should also be noted that the values of λ_0 should be taken lightly as this is essentially the value of the field distribution or Δ that is related to the muon hyperfine coupling with the nuclei moments. In TCNQ if one assumes a stopping site close to the nitrogen groups on one end where the radical electron density resides, then there is coupling to both the nitrogen and protons, if you swap the protons for fluorines then this will change the field distribution at the muon site. Coupled to the fact that there may multiple muon stopping sites, this may be especially complicated given that in the fluorinated compounds you have small contributions of F-μ^+-F states[46]. This will be discussed further in a subsequent manuscript but within this work, it need not be focused on.

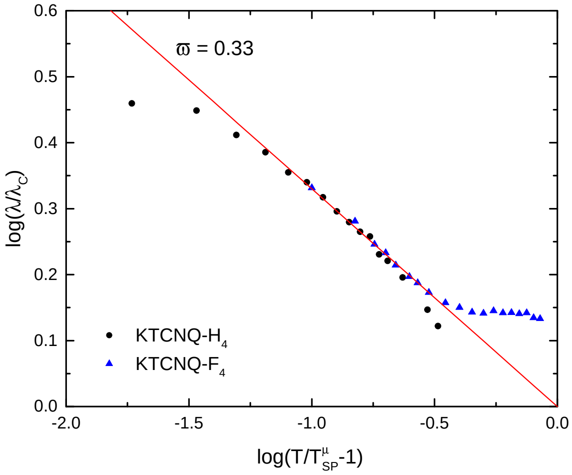

FIG. 4. Plots to illustrate the dynamic critical exponent (ϖ) calculated from fit to the scaled data. Note: the λ scale has been normalised by the value of the intercept ($\lambda_c = 0.098(3)$ and 0.108(2) μs^{-1} for the protio and fluoro samples respectively) in the linear plot for both samples showing the dramatic agreement across the critical region in both samples.

One advantage of ZF-μSR is the ability to track out order parameters and critical scaling behaviour[47] from both static order and spin dynamics. To gain a good estimate of the dynamic order parameter in both the protio and fluoro compounds the temperature data were scaled using sensible values of T^{μ}_{SP}; 324 K and 100 K for the protio and fluoro samples respectively. These values were then kept fixed throughout the analysis. In the protio sample, this value was approximately the value at the steepest slope, and for the fluoro sample, the steepest slope was not clearly identified and so a low estimate was taken between 90 K where the stretched exponential function could not reliable fit the data and 110 K where the onset of the SP transition is observed in the presented data. Using the behaviour of λ through a transition one is able to determine the dynamical exponent, ϖ, where $\lambda = \lambda_c(T/T^{\mu}_{SP} - 1)^{-\varpi}$. Within other SP systems the critical order parameter (applicable when $T < T_{SP}$) has been shown to be approximately 0.36 which corresponds to a Heisenberg 3D magnet[48–50]. In our case the dynamic exponents (applicable when $T > T_{SP}$), which is related to the critical slowing down of magnetic fluctuations within the paramagnetic state, are 0.33(1) and 0.332(9) for the protio and fluoro samples respectively and thus can be considered within error to be 0.33, which corresponds to a 3D Heisenberg system that is antiferromagnetically coupled[47]. In other systems[48–50], they were not able to distinguish between ferromagnetic and antiferromagnetic order however our results suggest that, for an SP system, the temperature dependent spin fluctuations appear to behave as if the system was approaching an antiferromagnetic state. If one considers that the muon is very strongly coupled to a TCNQ dimer, which falls into a singlet or antiferromagnetic groundstate, then this may begin to explain the exponent calculated. Since the SP transition in the M^+TCNQ^- salts are 3D both a structural and magnetic transition are congruent. Thus it may not be a surprise that the dynamic exponent points to a 3D transition that has an antiferromagnetic character as the magnetism is strongly bound to the behaviour of the lattice.

Within this paper it has been shown that the simple charge-transfer SP system, KTCNQ, can be easily tuned by substituting the aromatic protons for other atoms (or indeed other functional groups), demonstrated here with the substitution of H using four F. This is illustrated in the magnetic susceptibility data presented where the use of $TCNQF_4$ shifts the Peierls and SP distortion to approximately 165 K. Muon spin relaxation experiments showed a similar behaviour to that observed by Lovett *et al.*[33] where the relaxation was dominated by magnetic fluctuations and at low T the sample entered a quasi-static state. Although we see differences in spin gap energies, this difference may be due to the fact that susceptibility measurements are conducted in an applied fields, whereas μSR measurements are collected in a true zero-field environment. We have also been able to infer an estimate as to the critical nature of the transition from the muon data. Overall this work has shown how easily one can alter the TCNQ-TCNQ interactions within a strongly π-stacked salt such as this simple charge transfer salt. Substituting the protons on the aromatic ring for fluorine atoms will change the spin density across the TCNQ and ultimately this is likely to be behind the dramatic shift in T^{μ}_{SP} and T^{χ}_{SP}. It is hoped this illustrates how future work could begin to use this method for achieving desired magnetic properties through design.

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