

Supplementary Information

Exploring electron spin dynamics in spin chains using defects as a quantum probe.

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S1. DMRG CALCULATIONS

The simulations of the quantum systems were carried out using tensor networks and the Density Matrix Renormalisation Group (DMRG) method [1]. The tensor network calcula-

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tions were performed using the Python library `TENPY` [2]. It is important to note that DMRG is an approximation of the true ground state. There can be potential issues with convergence and small numerical errors, DMRG has shown its robustness for 1D non frustrated system. The SVD cut-off was set to 10^{-10} , while the convergence criterion for the ground energy was a relative change of 10^{-10} . We have calculated the ground state and sometimes the 1st excited state. Thanks to `TENPY`, the scripts run smoothly from some seconds to some minutes on the heavier calculation on an Apple macbook pro 2021 M1Max with 64Go of RAM.

While changing the value of δ we have computed the distribution of magnetization for an odd number of spin chain (see Fig. S1). It is worth to notice that for $\delta = \pm 1$ which correspond to uncoupled dimer, the local magnetisation is zero excepted at the site immediately after the defect. When decreasing $\|\delta\|$ the polarization spreads until $\delta = 0$ (*i.e.* the uniform spin chain) where the magnetization is now through the entire chain.

In order to estimate the effect of the dimerization factor δ on the dipol-dipol interaction between two edge state, we have calculated the triplet gap between two 51 spins chains connected to an Ising interaction of value d . In the non interacting case: $\delta = 1$ the coupling is only between the 2 isolated spin at the end. We can see that the dipol-dipol remains unchanged ($d_{eff} = d$). on the contrary in the case of uniform spin chain ($\delta=0$) the effective dipolar field tend to be extremely reduced ($d_{eff} \sim 0$). In the case of $(o\text{-DMTTF})_2X$, δ is close to 0.1 and $d_{eff} \sim 0.3$

S2. SPIN-PHONON INTERACTIONS

To understand the processes involved in spin relaxation process, it is essential to distinguish three subsystems: the spins, the lattice, and a thermal reservoir referred to as the bath [3]. The spins interact with lattice phonons via spin-orbit coupling: the lattice vibrates. The lattice and the bath exchange heat through thermal contact. The lattice has a low heat capacity, while the bath, by definition, has an infinite capacity. If the thermal contact between the bath and the lattice is efficient, they remain in thermal equilibrium $T_p = T_0$. This assumption is valid for describing the direct, Orbach, and Raman processes.

When the bath and the lattice exchange heat poorly, phonon-bath relaxation becomes non-negligible compared to spin-phonon relaxation. The lattice phonons, being few in number, heat up to a temperature $T_p \neq T_0$ and slow down spin-lattice relaxation. This phenomenon is called the "phonon bottleneck" [4].

S2.1. Direct Process

Consider a two-level magnetic system $\{|a\rangle, |b\rangle\}$ separated by the Zeeman energy $E_z = g\mu_B H_0$. The direct relaxation process results from the absorption and emission of a lattice phonon with energy $\delta = \hbar\omega = g\mu_B H_0$. Here, it is assumed that the lattice and bath are in continuous equilibrium. The spin populations n_a and n_b of each level evolve according to equation (S1), where $w_{a \rightarrow b}$ is the transition probability from state $|a\rangle$ to state $|b\rangle$ per unit time, and vice versa for $w_{b \rightarrow a}$.

$$\frac{dn_b}{dt} = -\frac{dn_a}{dt} = w_{a \rightarrow b}n_a - w_{b \rightarrow a}n_b \quad (\text{S1})$$

The spectral density of the phonon population $\rho(\omega)$ is given by equation (S2), where $g_D(\omega)$ represents the Debye density of states in three-dimensional space, and v is the speed of sound in the medium [5]. K is a temperature-independent coefficient.

$$\rho(\omega)d\omega = g_D(\omega)\bar{p}_0(\omega)d\omega \quad (\text{S2})$$

$$g_D(\omega) = \frac{3\omega^2}{2\pi^2 v^3} ; \bar{p}_0(\omega) = \frac{1}{e^{\hbar\omega/k_B T_0} - 1} \quad (\text{S3})$$

$$w_{b \rightarrow a} = K[1 + \bar{p}_0(\omega)] ; w_{a \rightarrow b} = K\bar{p}_0(\omega) \quad (\text{S4})$$

Introducing $n = n_- - n_+$ as the difference between the spin populations and $N = n_- + n_+$ as the total spin population, and combining equations (S1) and (S4), we derive:

$$\frac{dn}{dt} = 2K[-n_+\bar{p}_0(\omega) - n_+ + n_-\bar{p}_0(\omega)] \quad (\text{S5})$$

$$\frac{dn}{dt} = K[(1 + 2\bar{p}_0(\omega))n - N] \quad (\text{S6})$$

In equation (S5), we can identify, in sequence, stimulated emission, spontaneous emission, and the absorption of a phonon with energy $\hbar\omega$. At equilibrium, $T_s = T_0$ and $n = n_0 = N \tanh\left(\frac{\hbar\omega}{2k_B T_0}\right)$ is the thermal equilibrium polarization.

$$\frac{dn}{dt} = -\frac{1}{T_{1d}}(n - n_0) \quad (\text{S7})$$

From this, the temperature dependence of T_1 in the case of the direct process is deduced (S8). The coefficient K can be determined from $g(\omega)$ and by calculating the transition probability using perturbation theory [4]. For a Kramers doublet, the relation (S8) is found:

$$\frac{1}{T_{1d}} = \alpha_D g^3 B^5 \coth\left(\frac{\hbar\omega}{2k_B T}\right) \quad (\text{S8})$$

since our base temperature is 5.5K, $\hbar\omega \ll 2k_B T$ and we can approximate $\coth\left(\frac{\hbar\omega}{2k_B T}\right) \approx \frac{2k_B T}{\hbar\omega}$ and so at the resonance

$$\frac{1}{T_{1d}} = \alpha'_D B_0^4 T \quad (\text{S9})$$

for a Kramers doublet.

S2.2. Resonant Two-Phonon Process: Orbach

In the Orbach-type process, we consider a third energy level $|c\rangle$ separated by Δ_O from the level $|b\rangle$ and by $\Delta_O + \delta$ from the fundamental level $|a\rangle$. This process can only exist under the condition $\Delta_O < k_B \theta_D$, where θ_D is the Debye temperature [6, 7]. The transition

from state $|b\rangle$ to $|a\rangle$ occurs in two steps: absorption of a resonant phonon with energy Δ_O and emission of a resonant phonon with energy $\Delta_O + \delta$, as shown in figure S3.

$$w_{b \rightarrow c} = B[1 + \bar{p}_0(\Delta_0)] ; w_{c \rightarrow b} = B\bar{p}_0(\Delta_0) \quad (\text{S10})$$

$$w_{a \rightarrow c} = B[1 + \bar{p}_0(\Delta_0 + \delta)] ; w_{c \rightarrow a} = B\bar{p}_0(\Delta_0 + \delta) \quad (\text{S11})$$

$$\begin{cases} \frac{dn_a}{dt} = B[n_c(\bar{p}_0(\Delta_0 + \delta) + 1) - n_a\bar{p}_0(\Delta_0 + \delta)] \\ \frac{dn_b}{dt} = B[n_c(\bar{p}_0(\Delta_0) + 1) - n_b\bar{p}_0(\Delta_0)] \end{cases} \quad (\text{S12})$$

In many cases, the spin population of the third energy level can be considered small compared to the other two, $n_c \ll n_b, n_a$, and $\delta \ll \Delta_0$. The system of equations (S12) simplifies, and similarly to the direct process subsection S2S2.1, we find:

$$\frac{dn}{dt} = -1/T_{1O}(n - n_0) \quad (\text{S13})$$

It can be shown that for a Kramers doublet, T_{1O} follows the relation (S14):

$$1/T_{1O} = \alpha_o \Delta_0^3 e^{-\Delta_0/T} \quad (\text{S14})$$

S2.3. Non-Resonant Two-Phonon Process: Raman

The Raman process corresponds to the simultaneous absorption of a phonon with energy δ_1 and the emission of a phonon with energy $\delta_2 = \delta_1 + \delta$ to achieve a spin flip from $|b\rangle$ to $|a\rangle$. Unlike the Orbach process, the phonons are not constrained by the value of the gap Δ_O , and if $\delta \ll k_B\theta_D$, then the entire phonon energy spectrum is accessible up to θ_D . The only condition to satisfy is $\delta_2 - \delta_1 = \delta$. To calculate the transition probabilities per unit time $w_{b \rightarrow a}$ and $w_{a \rightarrow b}$, we consider $H_c^{(2)}$, the second-order perturbation of the spin-phonon coupling Hamiltonian. We then sum over all possible energies of δ_1 :

$$w_{b \rightarrow a} = \int \frac{2\pi}{\hbar} |\langle b, \bar{p}_0(\delta_1), \bar{p}_0(\delta_2) | H_c^{(2)} | a, \bar{p}_0(\delta_1) + 1, \bar{p}_0(\delta_2) + 1 \rangle|^2 \rho(\delta_2) \rho(\delta_1) d\delta_1 \quad (\text{S15})$$

$$w_{a \rightarrow b} = \int \frac{2\pi}{\hbar} |\langle a, \bar{p}_0(\delta_1) + 1, \bar{p}_0(\delta_2) + 1 | H_c^{(2)} | b, \bar{p}_0(\delta_1), \bar{p}_0(\delta_2) \rangle|^2 \rho(\delta_2) \rho(\delta_1) d\delta_1 \quad (\text{S16})$$

$$\frac{dn_b}{dt} = -\frac{dn_a}{dt} = K' \int n_a \bar{p}_0(\delta_2)(1 + \bar{p}_0(\delta_1)) - n_b \bar{p}_0(\delta_1)(1 + \bar{p}_0(\delta_2)) \delta_1^6 d\delta_1 \quad (\text{S17})$$

Similarly to the direct process section [S2S2.1](#), we find the equilibrium return equation ([S18](#)):

$$\frac{dn}{dt} = -\frac{1}{T_{1R}}(n - n_0) \quad (\text{S18})$$

$$\frac{1}{T_{1R}} = K'' \int_0^{\theta_D} \frac{\delta_1^6 e^{\delta_1/k_B T}}{(e^{\delta_1/k_B T} - 1)^2} \quad (\text{S19})$$

The integral ([S19](#)) can be simplified if we assume that the temperature T is low compared to the Debye temperature θ_D . This assumption is generally valid when measuring T_1 at temperatures close to liquid helium. In the case where the system is a Kramers doublet, we find the relation ([S20](#)):

$$1/T_{1R} = \alpha_R T^9 \quad (\text{S20})$$

The Raman process always exists, but the dependence of T_{1R} on temperature or magnetic field is strongly modified depending on the value of θ_D , the nature, or the size of the system [\[8\]](#).

S2.4. Phonon Bottleneck Effect

The phonon bottleneck effect manifests when the thermal contact between the lattice and the bath is poor. The lattice phonons are no longer necessarily in equilibrium with the bath at temperature T_0 [\[4\]](#). We now consider $\bar{p}(\omega)$ as the phonon population of the lattice at temperature T_p .

$$\bar{p}(\omega) = \frac{1}{e^{\hbar\omega/k_B T_p} - 1} \quad (\text{S21})$$

$$\frac{dn}{dt} = 2\rho(\omega)[n_b w_{b \rightarrow a}(\bar{p} + 1) - n_a w_{b \rightarrow a} \bar{p}] \quad (\text{S22})$$

$$\begin{cases} \frac{dn}{dt} = -\frac{1}{T_{1d}}[n - n_0 - n \frac{\bar{p} - \bar{p}_0}{\bar{p}_0 + 1/2}] \\ \frac{d\bar{p}}{dt} = -\frac{1}{\rho(\delta)\Delta\delta} \frac{dn}{dt} - \frac{\bar{p} - \bar{p}_0}{T_{ph}} \end{cases} \quad (\text{S23})$$

Faughnan and Strandbergh numerically calculated the solutions (S23) [9] and showed that $n(t)$ and $\bar{p}(t)$ are not monoexponential. They present a short relaxation time T'_{1b} and a long relaxation time T_{1b} , both of which can be expressed in terms of the bottleneck parameter σ .

$$T_{1b} = (1 + \sigma)T_{1d} \quad (\text{S24})$$

$$T'_{1b} = \frac{T_{ph}}{\sigma} \quad (\text{S25})$$

The bottleneck factor σ is very important. It is the ratio of the energy exchanged between the spins and the phonons relative to the energy exchanged between the phonons and the bath.

$$\sigma = \frac{E_z T_{ph}}{E_{ph} T_{SP}} = \frac{T_{ph} n_0}{T_{1d} \rho(\delta) \Delta\delta \coth(\frac{\delta}{2k_B T})} \quad (\text{S26})$$

When $\sigma \ll 1$, the bottleneck effect is not visible, so $T_{1b} = T_{1d}$, and the direct process correctly describes the spin relaxation. Conversely, when $\sigma \gg 1$, we speak of a severe bottleneck effect, and the measured relaxation time is significantly extended, $T_{1b} \simeq \sigma T_{1d}$. The relation (S27) is valid if $\delta \ll k_B T$:

$$T_{1b} \simeq \sigma T_{1d} = D \coth(\frac{\delta}{2k_B T})^2 \simeq D' T^2 \quad (\text{S27})$$

$$D' = \frac{6\Delta\delta k_B^2}{\pi^2 n v^3 \hbar^3 T_{ph}} \quad (\text{S28})$$

Faughnan and Strandbergh propose a simplified equation for $n(t)$ in the case $T_{1d} \gg T_{ph}$ (S29) [9]. This condition is generally satisfied. The equation (S29) has no trivial solution except for $\sigma = 0$, where $n(t)$ is an exponential law.

$$-\frac{t}{T_{1d}} = (1 + \sigma) \ln \left(\frac{n_0}{n - n_0} \right) - \sigma \frac{n}{n_0} \quad (\text{S29})$$

The solution $n(t)$ can be numerically calculated from equation (S29).

S2.5. Statistical Goodness of fit model

In The main text, we present spin lattice relaxation of $(o\text{-DMTTF})_2\text{Br}$, $(o\text{-DMTTF})_2\text{Cl}$ and $(o\text{-DMTTF})_2\text{I}$ using the chosen model (Orbach or Raman). Here we show the fit for both model confronted to every samples including error and R^2 estimation.

Table S1. Fitted parameters of spin lattice relaxation.

	Model	α_{R9} $\times 10^{-6}(\text{s}^{-1}\text{K}^{-9})$	α_O $\times 10^4(\text{s}^{-1}\text{K}^{-3})$	Δ_O (K)	R^2
$(o\text{-DMTTF})_2\text{Cl}$	Raman	13.1 ± 3.3	-	-	0.5085
	Orbach	-	1.13 ± 0.3	147 ± 4	0.9961
$(o\text{-DMTTF})_2\text{Br}$	Raman	1.1 ± 0.8	-	-	0.201
	Orbach	-	1.6 ± 0.4	181 ± 17	0.9851
$(o\text{-DMTTF})_2\text{I}$	Raman	4.17 ± 0.17	-	-	0.9889
	Orbach	-	0.0015 ± 0.0001	70 ± 2	0.4474

The value of R^2 clearly prove that Orbach process is involved in the relaxation of $(o\text{-DMTTF})_2\text{Cl}$ and $(o\text{-DMTTF})_2\text{Br}$ while Raman process dominates in $(o\text{-DMTTF})_2\text{I}$.

S2.6. Spin lattice relaxation of $(o\text{-DMTTF})_2\text{Cl}$ and $(o\text{-DMTTF})_2\text{I}$

The main text presents the spin lattice relaxation data of $(o\text{-DMTTF})_2\text{Br}$. Here we show the remaining systems.

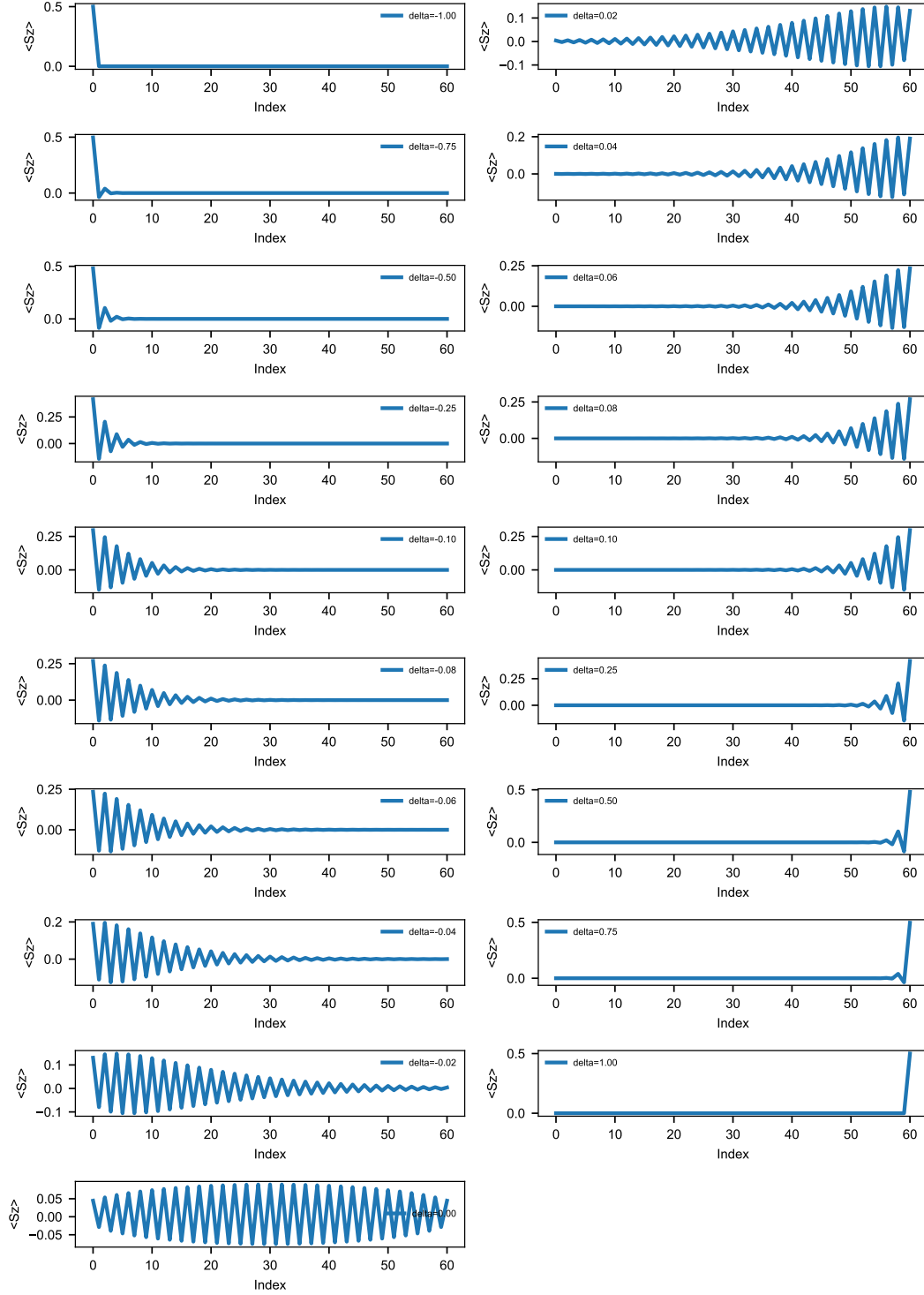


Figure S1. Spatial Magnetization Profiles for Open Spin Chains with Varying Dimerization. Local magnetization ($\langle S_z \rangle$) profiles, obtained through Density Matrix Renormalization Group (DMRG) calculations, are shown for open spin chains of $L=60$ sites. The dimerization parameter, δ , is varied across a range spanning from -1.00 to +1.00, including $\delta=0$ to represent the uniform spin chain. For each value of δ , the spin polarization arising from the open boundary conditions is clearly visible. These profiles illustrate the complex evolution of spin localization and correlation effects as the dimerization strength is modulated, transitioning from a regime of strong spin localization at the ends for large $|\delta|$ to a more homogeneous spin distribution for small $|\delta|$. Note that the edge polarization diminishes in magnitude as $|\delta|$ approaches zero.

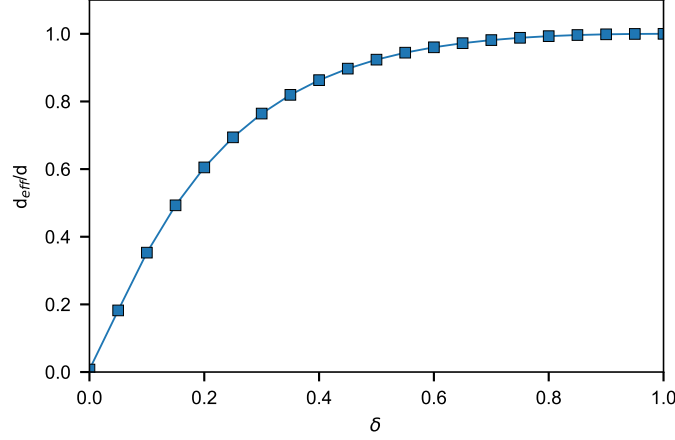


Figure S2. Effective dipole-dipole coupling between two quantum spin chain edge states (QSC-ES) as a function of the dimerization parameter δ , computed using DMRG. Two open spin chains of 51 sites each are coupled through an Ising-like dipolar interaction of value d . The effective dipolar coupling d_{eff} is extracted from the anisotropic triplet gap. In the limit $\delta = 1$ (chains of non-interacting dimers with an isolated spin at the end), $d_{\text{eff}} = d$, recovering the isolated-spin result. As δ decreases toward the uniform chain limit ($\delta = 0$), d_{eff} is strongly suppressed. For the values characteristic of $(o\text{-DMTTF})_2X$ ($\delta \approx 0.08\text{--}0.096$), we obtain $d_{\text{eff}} \approx 0.3d$, consistent with the reduction of the effective spin concentration observed experimentally by instantaneous diffusion.

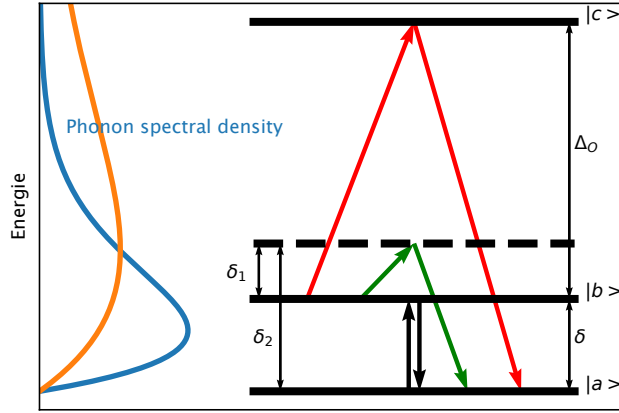


Figure S3. Schematic diagram illustrating the three subsystems involved in spin-lattice relaxation and the phonon bottleneck effect. The spin system exchanges energy with the lattice phonons via spin-phonon coupling. The lattice phonons, in turn, exchange heat with the thermal bath (reservoir at temperature T_0) through phonon-bath thermal contact. When thermal contact between the lattice and the bath is efficient, phonons remain at temperature $T_p = T_0$, and the standard direct, Orbach, or Raman relaxation processes apply. When this contact is poor, the phonons heated by the spin system reach a temperature $T_p \neq T_0$, slowing down the effective spin-lattice relaxation — a phenomenon known as the phonon bottleneck effect [4]. The three possible spin-lattice relaxation processes (direct one-phonon, resonant Orbach, and non-resonant Raman) are represented by arrows between the spin energy levels.

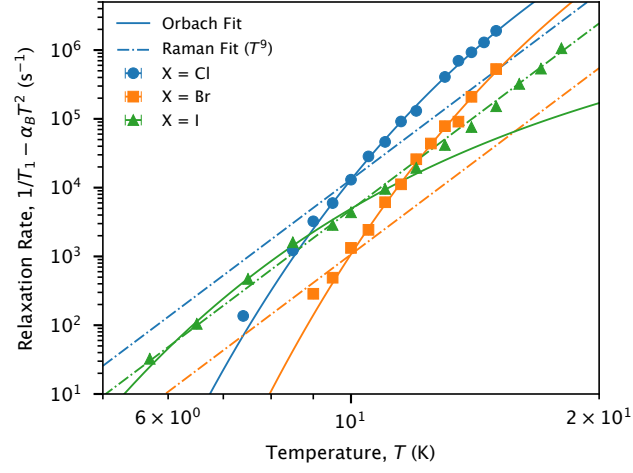


Figure S4. Spin lattice relaxation rate corrected by the phonon-bottleneck process presented in log-log scale. For the three compounds we have fitted using the two possible model : Orbach (plain line) and Raman (dashed dot line) processes

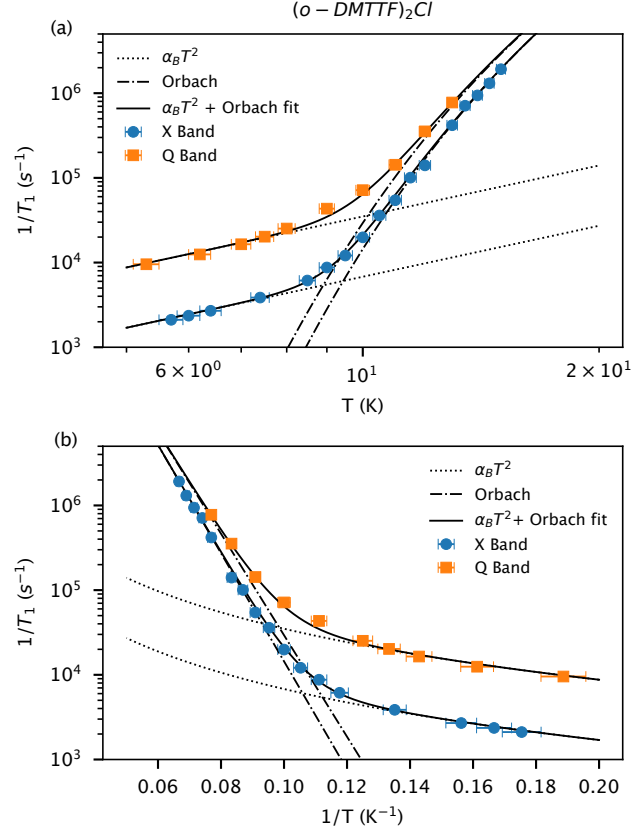


Figure S5. Temperature dependence of the inverse stretched relaxation time ($1/T_1^{\text{str}}$) for $(o - \text{DMTTF})_2\text{Cl}$, plotted against temperature (a) or the inverse of temperature (b) in a log-log scale, and measured at two microwave frequencies: X-band (9.7 GHz) and Q-band (34 GHz). The data are obtained via inversion recovery experiments at variable temperatures between 6 K and 20 K. The dashed lines represent the high temperature Orbach process and the dot line the phonon-bottleneck direct process. The plain black line is the sum of the two contribution

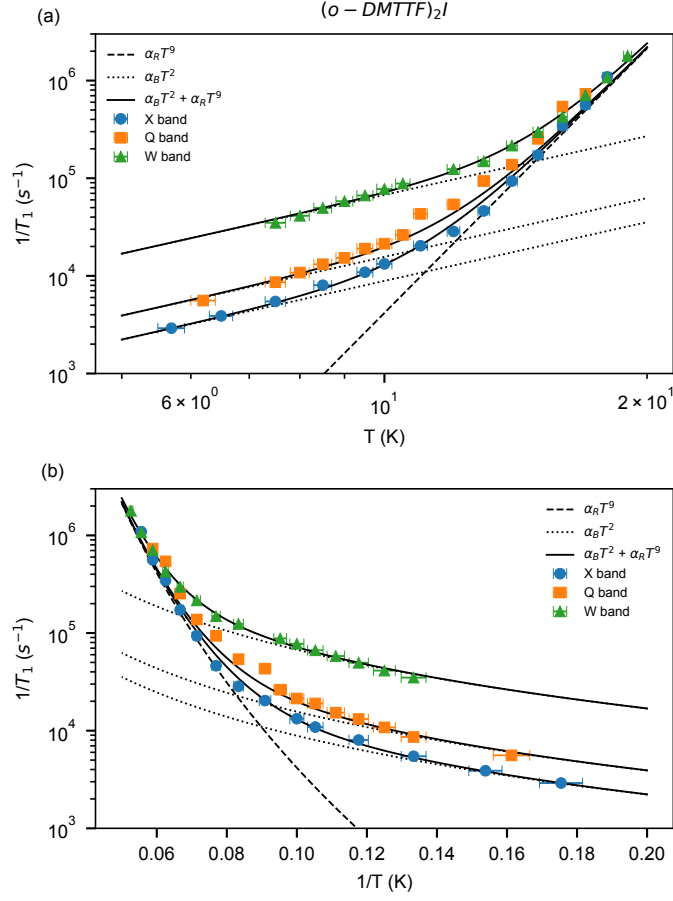


Figure S6. Temperature dependence of the inverse stretched relaxation time ($1/T_1^{\text{str}}$) for $(o\text{-DMTTF})_2\text{I}$, plotted against temperature (a) or the inverse of temperature (b) in a log-log scale, and measured at three microwave frequencies: X-band (9.7 GHz), Q-band (34 GHz), and W-band (94 GHz). The data are obtained via inversion recovery experiments at variable temperatures between 6 K and 20 K. The dashed lines represent the high temperature Raman process and the dot line the phonon-bottleneck direct process. The plain black line is the sum of the two contribution

S3. INSTANTANEOUS DIFFUSION

The main text introduces instantaneous diffusion as a significant decoherence mechanism affecting the Hahn echo decay. It outlines the theoretical basis where the coherence time T_2 is shown to depend on the refocusing pulse angle (θ_2) due to ID. While the main text features a detailed analysis of ID for (*o*-DMTTF)₂I (Fig. 6), this section provides the equivalent experimental two-pulse echo (2PE) decay measurements and the fitting according to Eq. (12) for the (*o*-DMTTF)₂Cl and (*o*-DMTTF)₂Br systems (shown in Figures S7 to S10). Figures S7, S8 and S9 display the raw 2PE decays for various refocusing pulse durations (t_p , which is proportional to θ_2), from which individual T_2 values are extracted. Figure S10) then shows the plots of $1/T_2$ versus the refocusing pulse parameters for chloride and bromide, analogous to Figure 6 for the iodide compound. In our experiment $\pi/2 = 24$ ns and θ_2 was set by changing the pulse time from 8ns every 2ns

Concentration calculation procedure

In the main text we compare two concentration values for each compounds. One obtained from a previous work [10] by continuous wave EPR (C_{cw}) and one obtained from instantaneous diffusion C_{ID} (present work). Here are details of the procedures: We start with the concentration in "defects per formula unit" from [10], which was determined by fitting the intensity of the EPR line and is directly related to the static susceptibility. We convert this dimensionless value to a volumetric concentration (in cm^{-3}) using the molar mass of the (*o*-DMTTF)₂X compound and its crystallographic density, which is known accurately from X-ray diffraction data ([11]). The formula used is: ($C_{cw} = (\text{defects/formula unit}) \times (\rho \times N_A)/M$, where ρ is the density, N_A is Avogadro's number, and M is the molar mass. The main source of error comes from the fit of the EPR susceptibility data, which we estimated to be around 10% is due to the error in quantitative EPR. This estimation of error is classic in the quantitative EPR of isotropic S=1/2 spins.

Regarding C_{ID} obtained by instantaneous diffusion, the method is completely different. We measured the echo decay by increasing the refoculisation pulse length, then we fitted the decay time and the standard deviation error which is usually within 1% error. We then plot the inverse of the decay time as function of $\langle \sin^2 \theta \rangle$ and we have fitted the slope with an

error of about 4%.

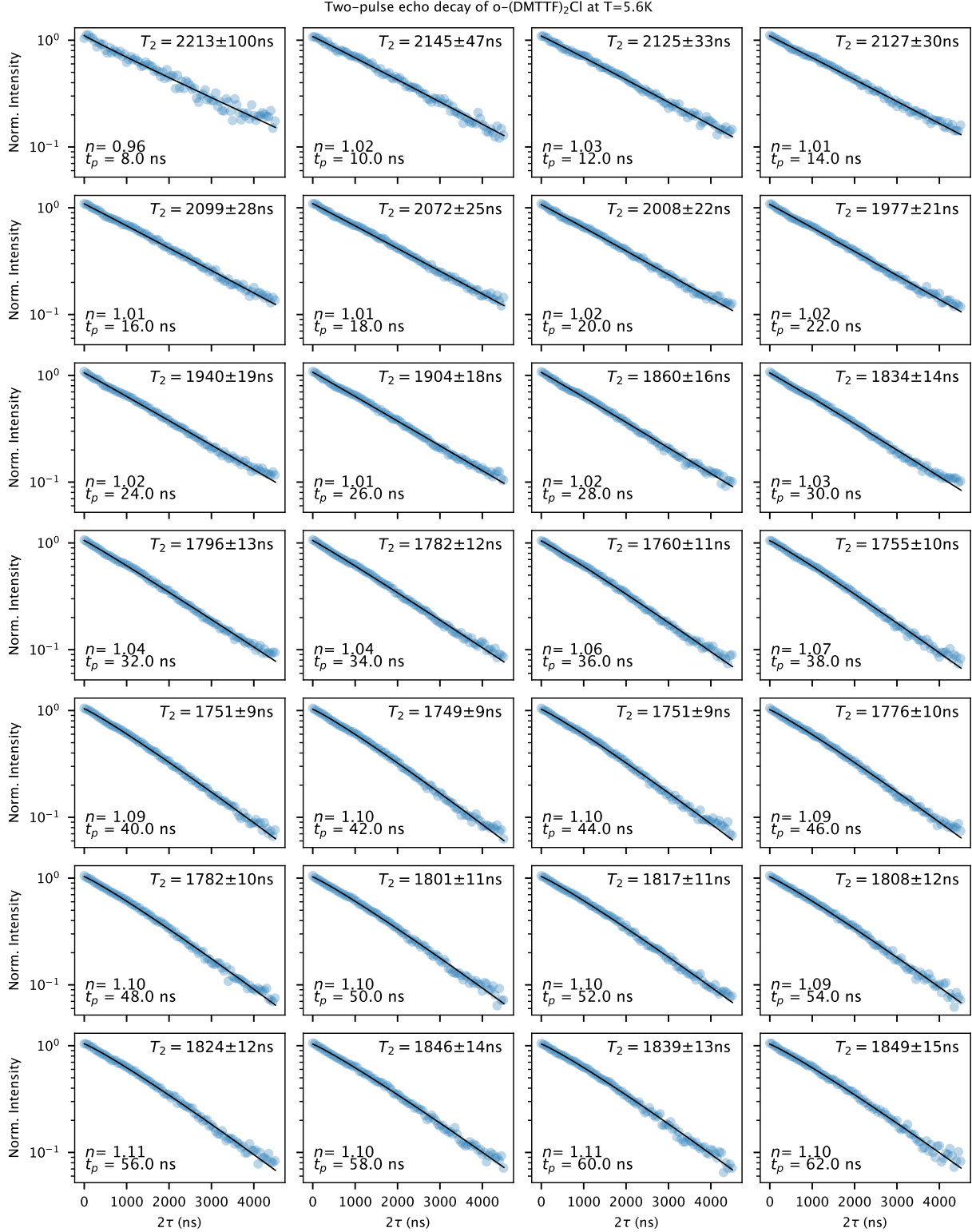


Figure S7. Two-pulse echo decay measurements for $(o\text{-DMTTF})_2\text{Cl}$ at $T = 5.6\text{K}$. The series of plots shows the decay of the spin echo signal as a function of the delay time τ between the excitation pulse ($\pi/2$) and the refocusing pulse (θ_2) induced by different durations (t_p) of the second pulse. These pulse durations are indicated in each graph, showing a change of decoherence rate for different duration pulse. Each solid blue lines corresponds to single exponential fits, resulting in the determination of T_2 values displayed at the top of each panel

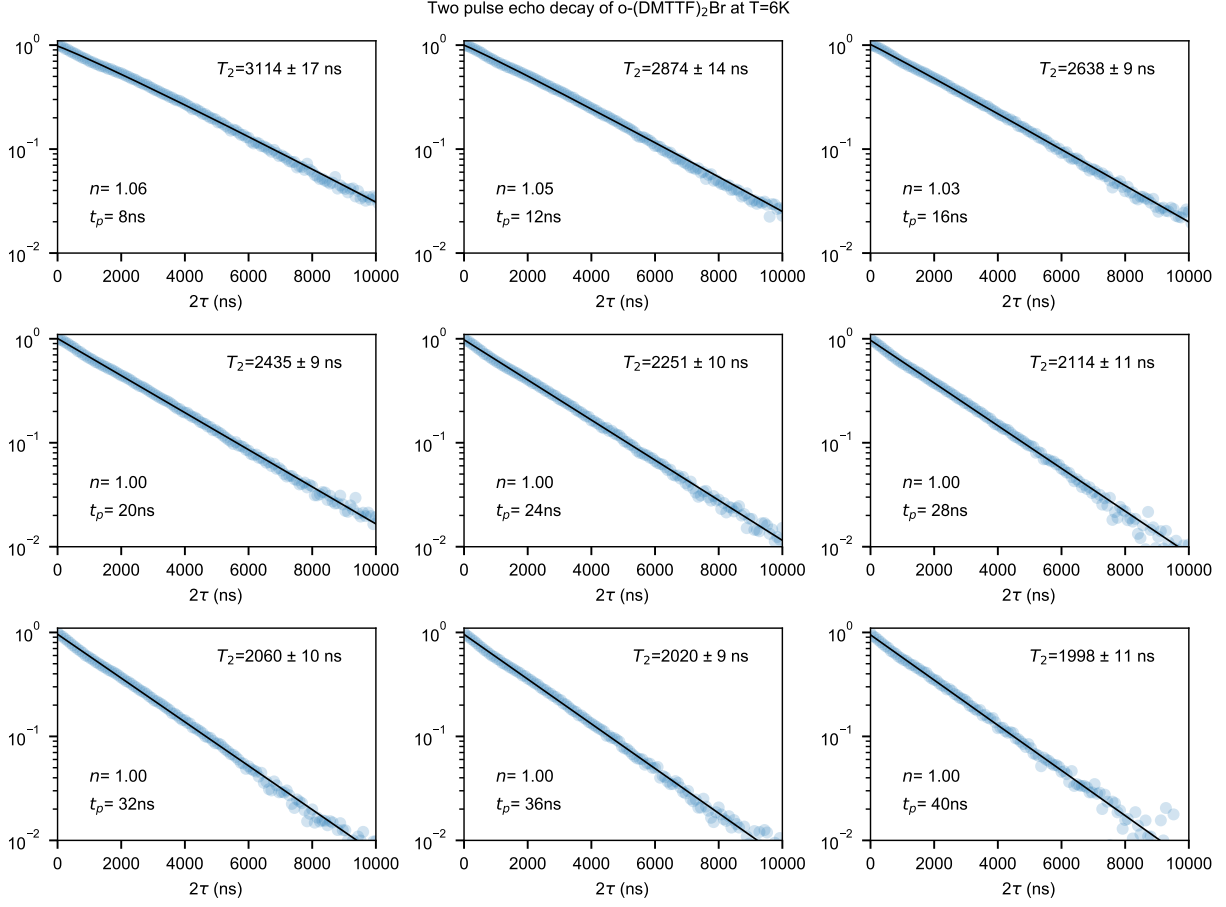


Figure S8. Two-pulse echo decay measurements for $(o$ -DMTTF)₂Br at $T = 6$ K. The series of plots shows the decay of the spin echo signal as a function of the delay time τ between the excitation pulse ($\pi/2$) and the refocusing pulse (θ_2) induced by different durations (t_p) of the second pulse. These pulse durations are indicated in each graph, showing a change of decoherence rate for different duration pulse. Each solid blue lines corresponds to single exponential fits, resulting in the determination of T_2 values displayed at the top of each panel

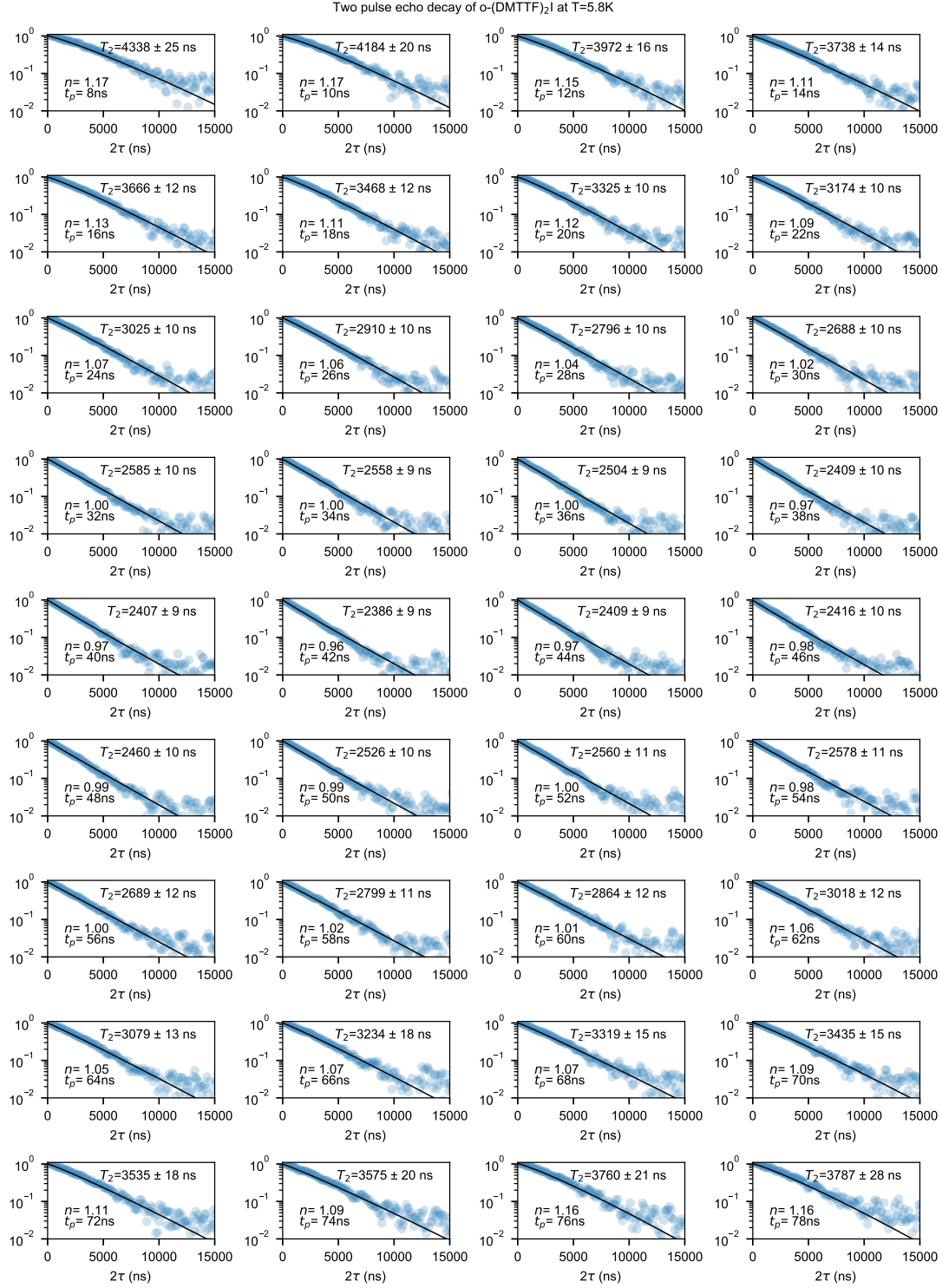


Figure S9. Two-Pulse Echo Decay Measurements for $(o\text{-DMTTF})_2\text{I}$ at 5.8 K with Varying Pulse Durations. A series of two-pulse Hahn echo decay curves are presented for $(o\text{-DMTTF})_2\text{I}$, measured at a temperature of 5.8 K. Each panel shows the decay of the spin echo signal amplitude as a function of the delay time (2τ) between the excitation pulse ($\pi/2$) and the refocusing pulse θ_2 . The duration of the refocusing pulse (denoted as t_p), is systematically varied for each decay series. The solid lines represent the best fits to the experimental data using a stretched exponential decay function, from which the coherence time (T_2) and the stretched parameter n is extracted.

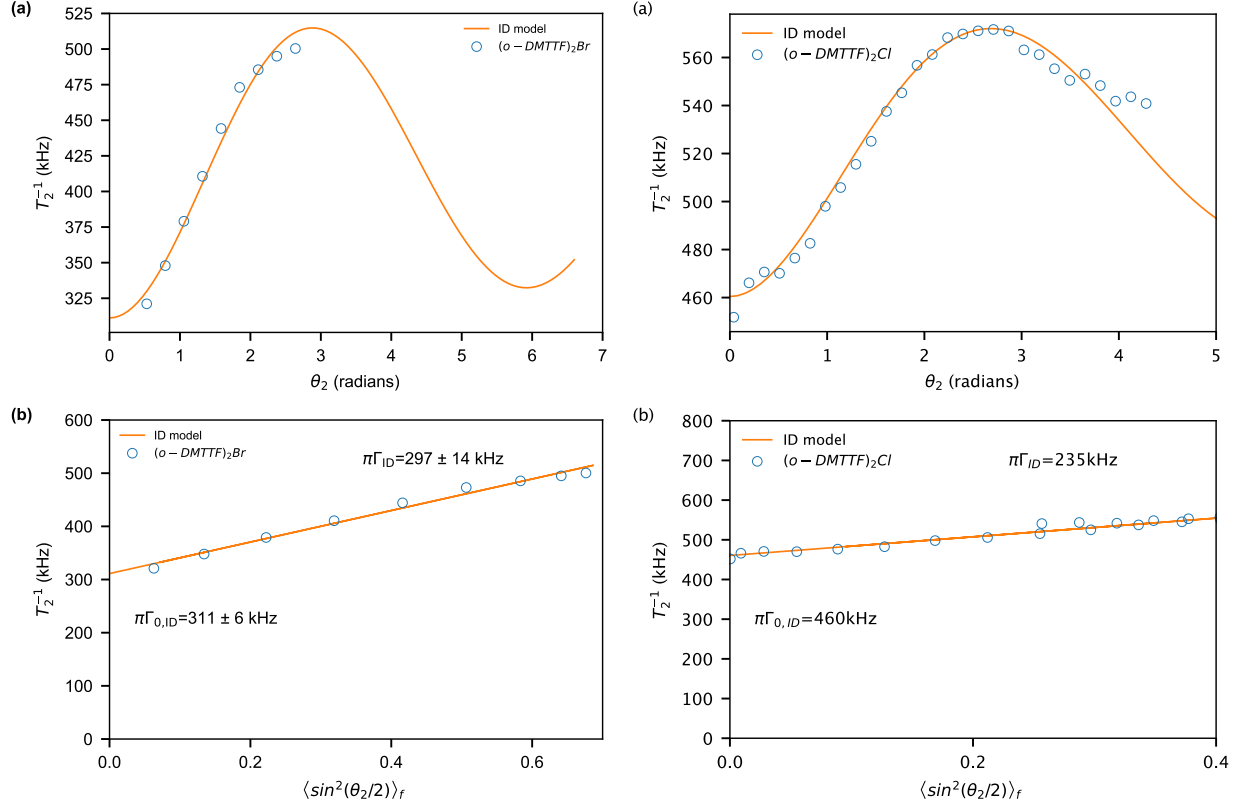


Figure S10. Two-Pulse Echo Decay Measurements for $(o\text{-DMTTF})_2\text{Br}$ (a) and $(o\text{-DMTTF})_2\text{Cl}$ (b). This figure presents a series of two-pulse echo decay curves using the same protocol as Fig. 6 of the main text. Each plot illustrates the decay of the spin echo signal amplitude as a function of the delay time (2τ) between the excitation pulse ($\pi/2$) and the refocusing pulse (θ_2). The refocusing pulse duration (t_p) is systematically varied to observe changes in the decoherence rate. Solid lines represent the best fits to the experimental data using Eq. (11)

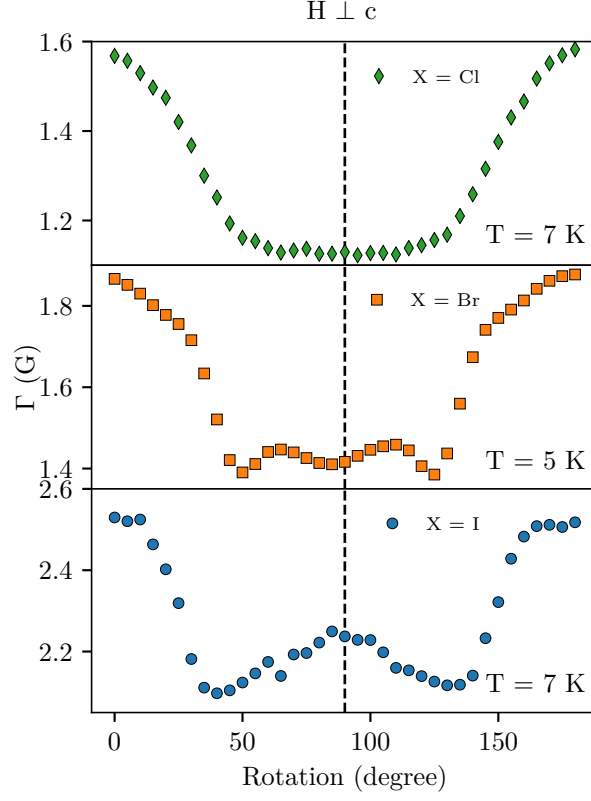


Figure S11. Angular dependence of the half-width at half-maximum (HWHM) Γ of the continuous-wave EPR line as a function of the orientation of the external magnetic field H_0 with respect to the crystal axes of $(o\text{-DMTTF})_2\text{I}$. The linewidth Γ is extracted from Lorentzian fits of the CW-EPR absorption spectra recorded at X-band (9.4 GHz) as a function of field angle. This angular dependence reflects the anisotropic nature of the spin Hamiltonian. The measured linewidth values are used directly in the computation of the instantaneous diffusion contribution to decoherence: specifically, the inhomogeneous linewidth Γ enters the evaluation of $\langle \sin^2(\theta_2/2) \rangle_f$ (Eq. (13) of the main text), which quantifies the fraction of spins effectively inverted by the refocusing pulse.

S4. SPIN-FLIP RATE

The spectral diffusion analysis reveals the crucial role of the spin-flip rate, denoted by R , in governing electron spin decoherence. This rate quantifies the frequency with which a spin in the surrounding environment, either electronic or nuclear, undergoes a transition that affects the local magnetic field experienced by the central, probed spin. The spin-flip rate, R , of group B spins acts as a key parameter within our theoretical model, describing the influence of the surrounding spin environment on the probed electron spin. Physically, this rate reflects the frequency at which spins in the environment undergo transitions, such as spin-lattice relaxation or flip-flops, thereby changing the local magnetic field and contributing to decoherence of the central spin. Our analysis of the spin-flip rate assumes, for simplicity, an isotropic g-factor. In this case, the spin flip rate can be decomposed into contributions from two distinct processes: spin-lattice relaxation (with rate $1/T_1$) and flip-flops (with rate R_{ff}). The spin-lattice relaxation process is mediated by phonons and is characterized by the interaction of the spin with the lattice vibrations, and is described by the Fermi Golden Rule. The flip-flop process, on the other hand, involves the mutual exchange of spin states between two or more interacting spins.

1. Spin-lattice flip rate

Relaxation is dominated by the direct phonon bottleneck process in our temperature range. If the perturbing spins are Kramers ions, their T_1 spin flip rate is

$$\frac{1}{T_1^{\text{phb}}} = \frac{3\omega^2\Delta\omega}{2\pi^2v^3n\tau_{\text{ph}}} \coth^2\left(\frac{\hbar\omega}{2k_{\text{B}}T}\right) \quad (\text{S30})$$

where v the velocity of sound in the crystal, $\Delta\omega$ is the resonance linewidth, n is the concentration of spins, and τ_{ph} is the lattice-bath relaxation time. Assuming $k_{\text{B}}T \gg \hbar\omega$, and the inhomogenous linewidth is field dependent we can simplify by

$$\frac{1}{T_1^{\text{phb}}} = \alpha'_B H_0 T^2 \quad (\text{S31})$$

2. Flip-flop rate

The flip-flop rate can be estimated following the analysis done in [12]:

$$R_{\text{ff}} \approx \frac{2\pi}{\hbar} \left(|\langle \uparrow\downarrow | H_{dd, \text{spin } i - \text{spin } j} | \downarrow\uparrow \rangle|^2 \right)_{\text{avg}} \frac{1}{\hbar \Gamma_{\text{inh}}} = \left(\frac{\pi \mu_0 \mu_B g^2 C}{9\sqrt{3}\hbar} \right)^2 \cdot \frac{1}{\Gamma_{\text{inh}}} \quad (\text{S32})$$

Using the concentration of QSD-EC and the linewidth of figure S11 we obtain :

$R_{\text{ff}} = 16.5$ kHz, 24.3 kHz and 14 kHz for $(o\text{-DMTTF})_2\text{Cl}$, $(o\text{-DMTTF})_2\text{Br}$ and $(o\text{-DMTTF})_2\text{I}$ respectively.

S5. ESTIMATION OF INTERNAL PROCESS IN THE DECOHERENCE

S5.1. Method of moments

In the case of pure random process, Anderson and Weiss [13] and Kubo et Tomita [14] have estimated that the sources of broadening which are included in the second moment of the distribution is reduced by the exchange interaction J.

The method of moments is a statistical technique used to analyze the shape and characteristics of spectral lines, particularly when the line shape is described by a Gaussian function. A Gaussian function is given by:

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$

where μ is the mean and σ is the standard deviation.

For a distribution f , the n -th moment about the mean is defined as:

$$M_n = \int_{-\infty}^{\infty} (x - \mu)^n f(x) dx$$

The second moment about the mean, measures the spread or width of the Gaussian spectral line:

$$M_2 = \int_{-\infty}^{\infty} (x - \mu)^2 f(x) dx = \sigma^2 \quad (\text{S33})$$

Considering the half width at half maximum of the distribution Γ_d , we obtain $M_2 = \Gamma^2/2 \ln 2$.

For electron electron interaction we obtain : $M_2^{e-e} = \left(\mu_0 \mu_B^2 g^2 C_{\text{tot}} / (9\sqrt{3}\hbar) \right)^2 / 2 \ln 2 \simeq$

$3 \times 10^{17} \text{Hz}^2$ where C_{tot} is the total concentration of spins

For anisotropic exchange interaction we used $M_2^{ani} = ((\Delta g/g)^2 J)^2$, using $\Delta g/g = 0.004$ and $J \sim 600 \text{ K}$ [10] we obtain $M_2^{ani} = 4 \times 10^{16} \text{Hz}^2$

S6. STRETCHED EXPONENTIAL

The stretched exponential function arises in systems where relaxation dynamics are influenced by a distribution of rates instead of a single relaxation process. Following Johnston article [15] let's summarize the main results. Experimentally we can fit the spin lattice relaxation using :

$$\langle S_z \rangle = \langle S_z \rangle_0 \exp \left[- \left(\frac{t}{T_1^{\text{str}}} \right)^\beta \right] \quad (\text{S34})$$

in the case of $0 < \beta < 1$ eq. (S34) becomes

$$\exp \left[- \left(\frac{t}{T_1^{\text{str}}} \right)^\beta \right] = \int_0^\infty P(s, \beta) e^{-s \frac{t}{T_1^{\text{str}}}} ds \quad (\text{S35})$$

where $s = \frac{T_1^{\text{str}}}{t}$ and $P(s, \beta)$ the probability density of s knowing β . In the particular case of $\beta = 1$, the relaxation is a monoexponential decay, $P(s, \beta = 1)$ is a Dirac function $\delta(s = 1)$ and $T_1^{\text{str}} = T_1$. For a general β , eq. (S35) is Laplace transform of $P(s, \beta)$ and consequently, $P(s, \beta)$ can be obtained by the inverse Laplace transform of the stretched exponential:

$$P(s, \beta) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} e^{-x^\beta} e^{sx} dx \quad (\text{S36})$$

Changing $u = -ix$, Johnston shown that

$$P(s, \beta) = \frac{1}{\pi} \int_0^\infty e^{-u^\beta \cos(\pi\beta/2)} \cos \left[su - u^\beta \sin(\pi\beta/2) \right] du \quad (\text{S37})$$

which can be evaluated numerically. Some examples are provided in Fig. S12. It is important to notice that the maximum of the distribution is not directly related to the data extracted relaxation time T_1^{str} . However, Johnston has shown that that $\frac{1}{T_1^{\text{str}}}$ is not the average relaxation rate but rather a characteristic property of the probability distribution $P(s, \beta)$. Specifically, $\frac{1}{T_1^{\text{str}}}$ is the value such that relaxation rates $\frac{1}{T_1}$ are about equally likely

to be less than $\frac{1}{T_1^{\text{str}}}$ as they are to be greater than $\frac{1}{T_1^{\text{str}}}$. This means $\frac{1}{T_1^{\text{str}}}$ can be interpreted as a median relaxation rate within the distribution of relaxation rates.

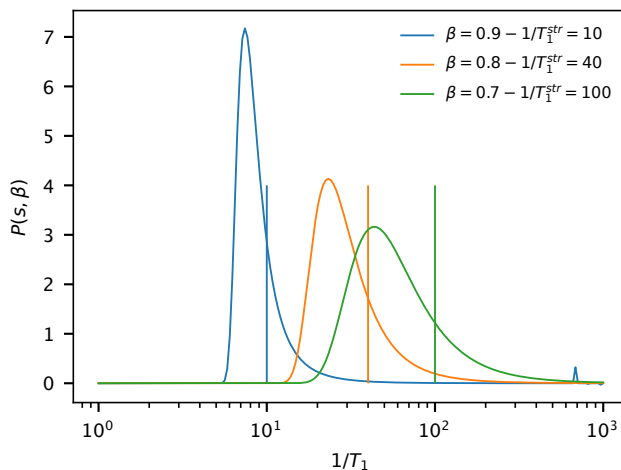


Figure S12. The probability density function, $P(s, \beta)$, which represents the distribution of relaxation rates (s), is shown for various stretched parameters: $\beta = 0.9$ with $1/T_{\text{str}} = 10 \text{ s}^{-1}$; $\beta = 0.8$ with $1/T_{\text{str}} = 40 \text{ s}^{-1}$; and $\beta = 0.7$ with $1/T_{\text{str}} = 100 \text{ s}^{-1}$. $P(s, \beta)$ was computed using Equation ((S37)), illustrating how different values of β and $1/T_{\text{str}}$ correspond to different distributions. A vertical line marks the input value of $1/T_{\text{str}}$ for each set of parameters to guide the eye.

DFT CALCULATIONS

Computational details

Theoretical calculations were based on the Density Functional Theory (DFT) and were performed using the ORCA 6.0 program [16–18]. To facilitate comparison between theory and experiment, the X-ray crystal structure of (o-DMTTF)₂/ was used. The DFT model includes two dimethylnitrotetrafulvalene units together with 6 bromine counter-ions. The hydrogen atoms of the DFT model were geometry-optimized while constraining the positions of other atoms to their experimentally derived coordinates. All calculations were carried out using the hybrid functional B3LYP [19, 20] and the x2c-TZVPall basis sets [21]. Relativistic effects were included using the exact two-component (X2C) Hamiltonian [22–24]. Tight convergence criteria were imposed using the TightSCF keyword along with the default (DefGrid2) integration grids. Dispersion correction was applied according to the method developed by Grimmer with the Becke-Johnson damping scheme (D3BJ) [25].

The spin-orbit coupling (SOC) operator was treated by a mean-field approximation to the Breit–Pauli operator (SOType 3 in ORCA) [26]. Construction of the effective potential included one-electron terms, the Coulomb term was computed with the RI approximation, exchange was incorporated via one-center exact integrals including spin-other orbit interactions, and local DFT correlation was included with VWN5 (all these choices are set with the keyword "SOCFlags 1,3,3,1" in ORCA).

Computational results

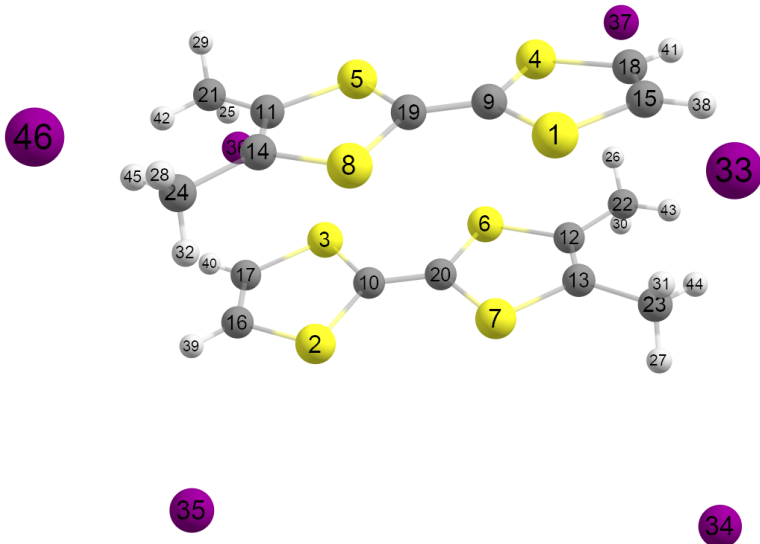


Figure S13. Atom labelling of the DFT model used for the hyperfine coupling constant calculations of $(o\text{-DMTTF})_2\text{I}$. The model consists of two $o\text{-DMTTF}$ units together with six bromine counter-ions, extracted from the X-ray crystal structure. Labels are assigned to all hydrogen atoms (H25–H45) whose hyperfine coupling constants are listed in Table S1. The sulfur, carbon, and bromine atoms are shown without labels for clarity. All DFT calculations were performed with the ORCA 6.0 program using the hybrid functional B3LYP with the x2c-TZVPall basis set and the exact two-component (X2C) relativistic Hamiltonian.

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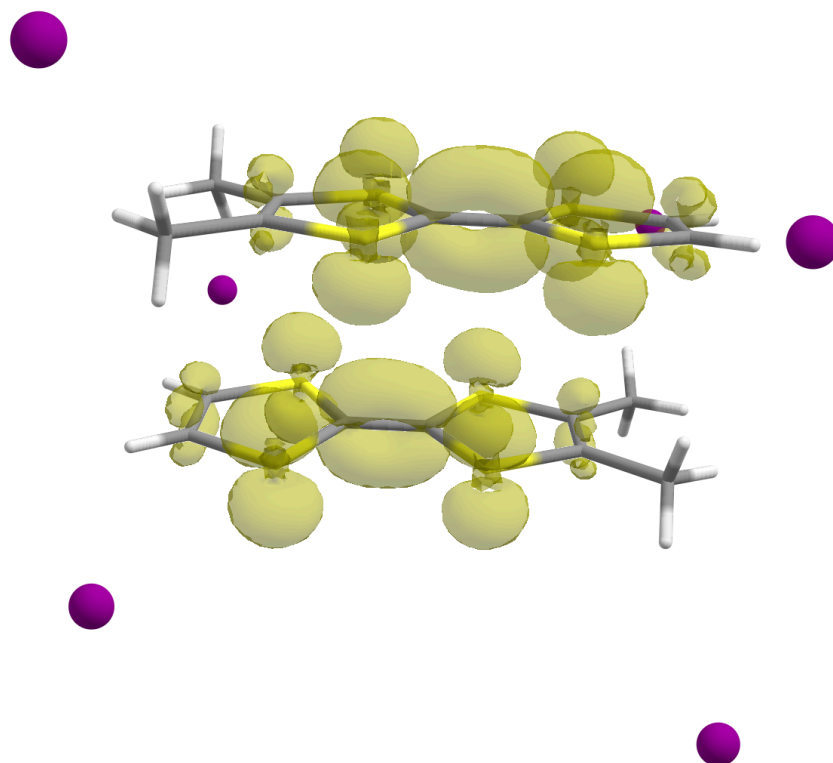


Figure S14. DFT-computed spin density plot of $(o\text{-DMTTF})_2\text{I}$, obtained at the B3LYP/x2c-TZVPall level of theory with the X2C relativistic Hamiltonian. The spin density is shown as an isosurface representation, with positive (excess α -spin) and negative (excess β -spin) contributions displayed in different colors. The spin density is predominantly delocalized over the two o -DMTTF molecular units, reflecting the charge-transfer nature of the salt and the partial oxidation of each o -DMTTF pair sharing one hole and one unpaired spin. The delocalized character of the spin density provides the basis for the estimation of the electron-nuclear dipolar second moment M_2^{e-n} used in the method-of-moments analysis of the homogeneous linewidth (Section S5 of the Supplementary Information). Bromine counter-ions carry negligible spin density.

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Table S2. DFT-computed hyperfine coupling constants (total values A_{ii} , and individual spin-dipolar components A_{ii}^{SD} , in MHz for (*o*-DMTTF)₂I

Center	A_{11}	A_{11}^{SD}	A_{22}	A_{22}^{SD}	A_{33}	A_{33}^{SD}	A_{iso}
H25	1.23	-0.74	1.74	-0.23	2.95	0.97	1.97
H29	1.04	-0.55	1.16	-0.42	2.58	0.98	1.59
H42	-0.38	-0.30	-0.73	-0.64	0.87	0.95	-0.08
H28	0.09	-0.52	0.25	-0.37	1.53	0.89	0.62
H32	0.54	-0.71	1.09	-0.17	2.15	0.88	1.26
H45	-0.25	-0.30	-0.50	-0.55	0.90	0.85	0.05
H38	0.44	1.66	-1.83	-0.53	-2.41	-1.13	-1.26
H41	0.25	1.83	-1.99	-0.37	-3.09	-1.46	-1.61
H39	0.44	1.66	-1.83	-0.53	-2.41	-1.13	-1.26
H40	0.25	1.83	-1.99	-0.37	-3.09	-1.46	-1.61
H26	1.23	-0.74	1.74	-0.23	2.95	0.97	1.97
H30	1.04	-0.55	1.16	-0.42	2.58	0.98	1.59
H43	-0.38	-0.30	-0.72	-0.64	0.87	0.95	-0.08
H27	0.09	-0.52	0.25	-0.37	1.53	0.89	0.62
H31	0.54	-0.71	1.09	-0.17	2.15	0.88	1.26
H44	-0.25	-0.30	-0.50	-0.55	0.90	0.85	0.05

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