Supplementary Material for

Experimental protection of the spin coherence of a molecular qubit exceeding a millisecond

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I. SAMPLE PREPARATION

We prepared the compounds **1Cu** and **1Ni** according to a literature procedure[1]. Bis- (tetraphenylphosphonium) - bis -(maleonitriledithiolato)cuprate $(PPh_4)_2[Cu(mnt)_2]$ (**1Cu**): Sodium malontriledithiolate (279 mg, 1.5 mmol) was dissolved in 5 ml ethanol and 2 ml demineralized water. Subsequently copper chloride dihydrate (128 mg, 0.75 mmol), dissolved in 5 ml ethanol, and tetraphenylphosphonium bromide (629 mg, 1.50 mmol), dissolved in 15 ml ethanol were added under stirring. The brown product precipitated immediately and was separated from the solution after 5 min by vacuum filtration. Washing of the product with 3×5 ml ethanol and drying for 20 hours under reduced pressure. Bis-(tetraphenylphosphonium)-bis-(maleonitriledithiolato)nickelate $(PPh_4)_2[Ni(mnt)_2]$ (**1Ni**): The same procedure as described for **1Cu** was executed with nickel chloride hexahydrate (178 mg, 0.75 mmol) instead of copper chloride dihydrate. Doped powder: 0.3% of **1Cu** in **1Ni**: Doped powders were obtained by dissolving compounds **1Cu** and **1Ni** in the molar ratio 0.3 : 99.7 in a minimum volume of acetone, which was subsequently evaporated under reduced pressure. The resulting powders were dried in vacuo and finely ground. We characterize the samples by XRD spectroscopy and find that the experimental results are in good agreement with the numerical simulation as shown in the Fig. S1.

II. SIMULATION OF THE FSED

The fitting of the FSED is implemented by EasySpin[2], which is an open-source MATLAB toolbox for simulating Electron Paramagnetic Resonance spectra. We fit the FSED spectrum following the reference[2], yielding $g_{\parallel} = 2.0898$, $g_{\perp} = 2.0215$, $A_{\parallel} = 495.4$ MHz and $A_{\perp} = 118$ MHz.

III. T1 MEASUREMENT

The spin-lattice relaxation times T_1 is measured with inversion recovery method with the sequence $\pi - \tau_1 - \pi/2 - \tau_0 - \pi - \tau_0 - echo$ as shown in the inset of Fig. S2. The length of the π pulse is 48 ns. We show the T_1 measured at 9 K as an example in Fig. S2. The echo intensity follows an exponential relationship, $A_1 \exp[-(t/T_1)^{\beta_1} + B_1]$, where β_1 is the stretch factor. The result gives $T_1 = 14.4(3)$ ms.

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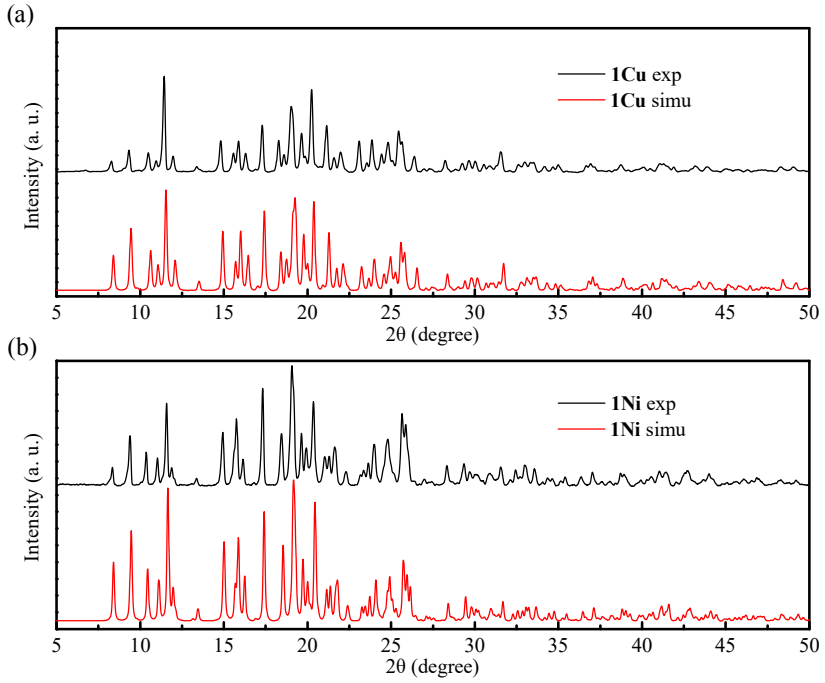

FIG. S1. (Color online). Powder X-ray Diffraction. XRD pattern of (a) **1Cu** and (b) **1Ni**. Black (red) lines denote the experimental (simulated) results.

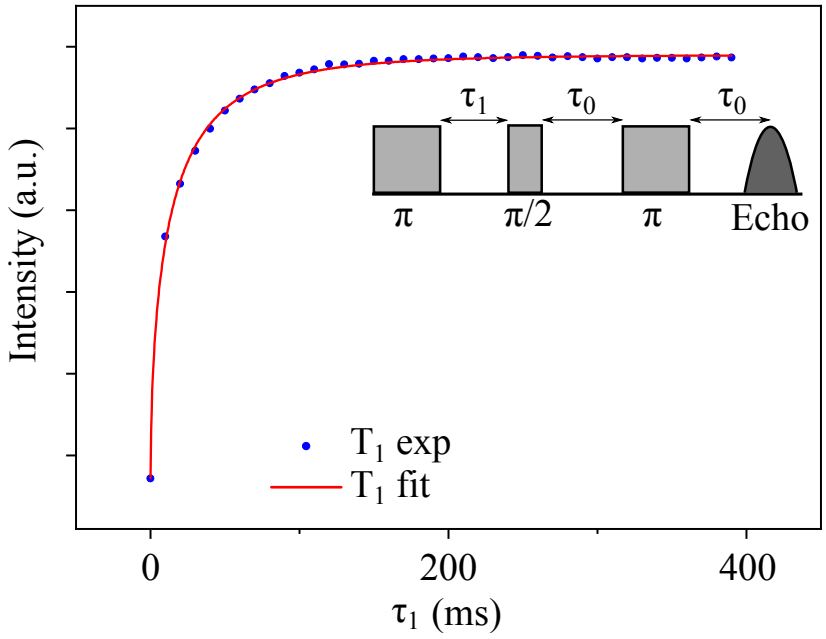

FIG. S2. (color online). T_1 measurement for **1Cu**. T_1 is measured to be 14.4(3) ms (blue dots) at 9 K. The red line is the exponential fitting of the experimental data. Inset shows the pulse sequence of the T_1 measurement.

IV. T2 MEASUREMENT

The T_2 is measured with spin echo sequence $\pi/2 - \tau_2/2 - \pi - \tau_2/2 - echo$ as shown in the inset of Fig. S3. The length of the π pulse is also 48 ns. Fig. S3 shows the T_2 measured at 9 K. The echo intensity follows an exponential decay, $A_2 \exp[-(t/T_2)^{\beta_2} + B_2]$, where β_2 is the stretch factor. The result gives $T_2 = 7.06(4)$ μs.

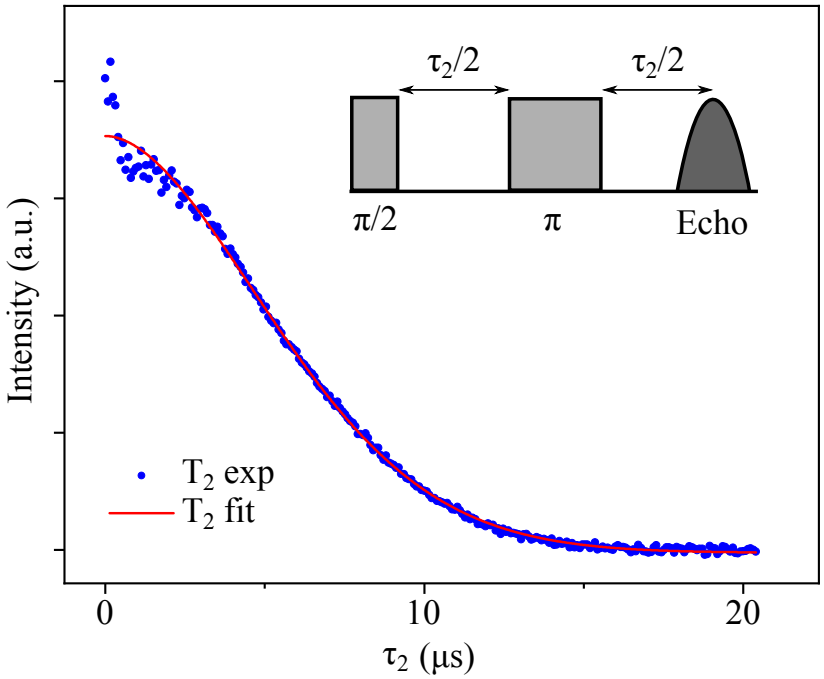

FIG. S3. (color online). T_2 measurement for **1Cu**. T_2 is measured to be 7.06(4) μs (blue dots) at 9 K. The red line is the exponential decay fitting of the experimental data. Inset shows the pulse sequence of the T_2 measurement.

V. SIMULATION OF THE CPMG EXPERIMENTAL RESULTS

The coherence decay of the **1Cu** molecular qubit is described in the general form $C(t) = e^{-\chi(t)}$, where the functional $\chi(t)$ describes the time dependence of the decoherence process[3]. In the present of the pulse sequence on **1Cu** molecular qubit, the decoherence functional is given by

$$\chi(t) = \frac{1}{\pi}\int_0^\infty d\omega S(\omega)\frac{F(\omega t)}{\omega^2}, \tag{1}$$

where the filter function $F(\omega t)$ characterize the pulse sequence in the frequency domain. The filter function of CPMG sequence depend on the number of pulses N and the distribution of π-pulses can be written as[4]

$$F(\omega t) = |1 + (-1)^{N+1}e^{i\omega t} + 2\sum_{j=1}^{N} e^{i\delta_j \omega t}\cos(\omega\tau_\pi/2)|, \tag{2}$$

where $\delta_j \in [0, 1]$ is the normalized position of the centre of the jth π-pulse between the two $\pi/2$-pulses, $t = N\tau$ is the total free-induction time and τ_π is the length of each π-pulse. The simulation of the coherence decay under CPMG experiment is done by treating the nuclear spin bath as the classical noise with a Gaussian noise spectral density coming from different nuclear spins. The total noise spectrum can be written as

$$S(\omega) = \sum_i A_i \exp(-(\omega - \omega_{Li})/2{\sigma_i}^2)/(\sigma_i\sqrt{2\pi}), \tag{3}$$

where $i \in \{\mathrm{H}, \mathrm{C}, \mathrm{P}\}$ corresponding to the molecule composition of **1Cu**. A_i, σ_i and ω_{Li} are the intensity, broadening and center frequency of each nuclear spin noise spectrum. The envelope of echo intensity $C(t)$ follows an exponential decay, $M = \exp[-(t/T_{coh})^\beta]$, where β is the stretch factor. When $N = 1$, the fitting result of β is 1.90. As N increases, β quickly approaches 1. In order to suppress the fitting error of T_{coh}, we lock β to 1 for fitting when $N \geq 8$. The modulation of the spin coherence is fitted by considering the filter function of the CPMG sequence $F(\omega t)$ and the noise spectral density $S(\omega)$. For the case of CPMG-4, the dips in the coherence decay are mainly induced by ^{1}H nuclear spins. There is a peak in the noise spectrum at the frequency 14.33 MHz, which matches the Larmor frequency of ^{1}H. The modulation depth is enhanced with the increasing of the number of π pulses in the CPMG sequence. The weak noise signals of ^{13}C and ^{31}P emerge, yielding two more peaks in the noise spectrum. Fig. S4 shows the simulation

result of 512 pulses. In this case, there are three peaks in the noise spectrum at the frequencies 14.33 MHz, 3.63 MHz and 5.81 MHz, which match the Larmor frequencies of ^{1}H, ^{13}C and ^{31}P, respectively. The simulation result agrees well with the experimental data. When more than 1000 DD pulses are applied, the quantum effect of the nuclear spin bath emerges and the negative spin coherence is observed. While the simulation process discussed above can only be used when the coherence is always positive. So the simulation of the CPMG-4 experiment does not apply to the case of the pulse number larger than 1000.

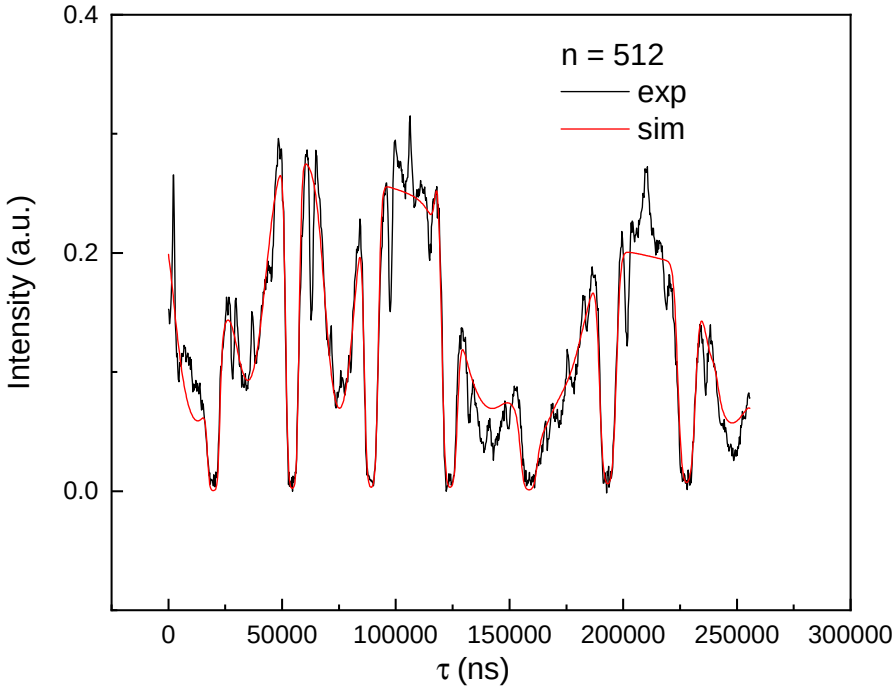

FIG. S4. (color online). Echo intensity decay under CPMG-512 pulse sequences. Dips of modulation in coherence decay are induced by ^{1}H, ^{13}C and ^{31}P nuclear spins. The simulation (red line) with effect of the nuclear spins is according with the experimental result (black line).

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