Supplementary Materials for

Optically pumped spin polarization as a probe of many-body thermalization

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This PDF file includes:

Sections S1 to S5
Figs. S1 to S8
I. Experimental

The experimental setup is a modified version of the system described in Ref. [15]. Briefly, it consists of a 400 MHz solid-state NMR magnet and spectrometer with a pneumatic shuttling device (Fig. S1A). During the hyperpolarization sequence, the sample is kept outside of the bore of the magnet, in the magnet’s stray field, at about 52.3 mT. An electromagnet, with current provided by a programmable power supply (GW Instek PSM-6003) is used to fine tune the magnetic field to the hyperpolarization condition (Fig. S1B). The sample is optically pumped at low field with a 532 nm laser with ~ 700 mW at the sample. The laser is pulsed with an AOM (acousto-optic modulator, Isomet 1250C) for time-resolved measurements. The beam diameter is adjusted using a lens just before the sample. The pneumatic shuttling system sends the sample to the magnet’s “sweet spot” in ~1s and a $^{13}$C FID is subsequently collected. The shuttling and spectrometer triggering are controlled with TTL pulses from a National Instruments DAQ card (PCIe 6321).

The NMR probe — which moves along with the sample — has been altered slightly from Ref. [15] to allow for manipulation of the $^{13}$C spins at low field in the hyperpolarization process. The RF is provided by an additional loop of wire near the sample. The loop terminates to either a 50-ohm resistor or shorts to ground to form a stub antenna depending on power needs. The RF signal is generated by a Rhode & Schwarz SMV 03 and amplified with a Minicircuits LZY-22+. Before amplification, the RF signal is gated by a switch (Minicircuits ZASWA-2-50DR+). Due to the bandwidth of the amplifier overlapping with the bandwidth of our spectrometer’s receiver, the blanking control line of the amplifier is used to reduce the noise level in the detected signal. The RF amplifier blanking is controlled by the DAQ card. For experiments requiring precise time resolution, the AOM and the gate for the MW switch are controlled with pulses from a SpinCore Pulseblaster-300.

The RF power is calibrated by detecting $^{13}$C Rabi oscillations (Figs. S1C and S1D). To this end, a hyperpolarization step is performed; the laser pumps the diamond for 10 seconds with the magnetic field tuned close to 52.3 mT to where the hyperpolarization is maximum. At the end of the pumping, just before the shuttling, an RF pulse, resonant with the $^{13}$C Larmor frequency is applied. The sequence is repeated 4 times and averaged. This is done for a range of RF pulse durations allowing us to extract the Rabi frequency and hence, the $B_1$ magnetic field amplitude. An oscilloscope is used to monitor the peak-to-peak voltage. The output of the signal generator is adjusted so as to maintain the peak-to-peak voltage unchanged for all frequencies used.
Experiments to determine the impact of different hyperfine coupled $^{13}$Cs (Fig. 2 in the main text) were performed by tuning the magnetic field to the positive or negative hyperpolarization features associated with the P1’s central Zeeman transition. For the present crystal orientation, this occurs slightly below or above 52.3 mT for the positive or negative polarizations ($B^+$ or $B^-$, in Fig. 1D of the main text). The AOM and RF switch are triggered both at the same time for a variable duration, typically 5-10 s. This is repeated several times (normally 8) for each RF frequency. When the RF excites a hyperfine coupled carbon, this shorts the hyperpolarization diffusion process, lowering the hyperpolarization signal. To characterize nuclear spin diffusion (Fig. 4 in the main text), a pulse sequence consisting of 2 ms laser pulses separated by a dark time with variable duration RF pulses is looped until 2 seconds of laser time has been accumulated and averaged 12 times per RF pulse duration. A reference with the same dark time and no RF pulse is taken to compare the impact of the RF pulse.

II. The spin Hamiltonian

The main goal in this and the following sections is to provide a quantum-mechanical model that qualitatively describes the polarization flow from strongly hyperfine-coupled $^{13}$Cs to bulk $^{13}$Cs. In order to simplify our formal description, we assume that the hyperfine-coupled carbons are initially polarized (by means of the NV-P1 energy

Figure S1. Stray-field optical pumping of $^{13}$C polarization in diamond. (A) Experimental setup. Dynamic polarization of $^{13}$C spins in diamond is carried out via optical excitation in the stray field of a superconducting NMR magnet (9.0 T). To detect the induced polarization, we shuttle the sample to the sweet spot of the magnet and acquire a free-induction-decay (FID) upon a resonant π/2-pulse at 96.87 MHz. (B) Example $^{13}$C NMR spectra upon 2-second optical excitation and a laser power of 0.7 W; the total number of repeats is 12 and spectra have been slightly displaced vertically for clarity. The signal is positive or negative depending on the exact value of the optical pumping field (see main text for details). From a comparison against the thermal signal amplitude at 9 T (24 repeats, upper inset) and the size of the illuminated spot (~100 µm), we conclude the dynamically pumped $^{13}$C polarization is of order 1-3%. (C) $^{13}$C spin manipulation at low field ($B^+ = 52.3$ mT) is carried out via RF excitation at a variable frequency prior to sample shuttling. As an example, the cartoon shows the schematics of a Rabi protocol at low field. (D) $^{13}$C NMR amplitude as a function of the RF pulse duration as obtained from the protocol in (C). The polarization field is $B^+ = 52.3$ mT and the RF frequency (560 MHz) is resonant with the bulk carbon Zeeman transition. The optical illumination time is 10 s and the number of repeats per point is 4.
matching mechanism discussed in Ref. [15]) and focus specifically on the spin-diffusion process. This means that we do not need to include the primary source of polarization, i.e. the NVs. The complete spin system therefore comprises \( N_S \) electrons (P1 centers) and \( N_I \) nuclear spins (\(^{13}\text{C}\)). The Hamiltonian describing this system is given by:

\[
H_T = \sum_{k,l} H_D(I_k, I_l) + \sum_{m,n} H_D(S_m, S_n) + \sum_{k} \gamma_1 B \cdot I_k + \sum_{m} \gamma_S B \cdot S_m + \sum_{k} \sum_{m} V_{\text{int}}(I_k, S_m) \quad (A.1)
\]

Here, the first term corresponds to the dipolar interaction between \(^{13}\text{C}\) nuclear spins, the second is the dipolar interaction between P1 centers, the third and fourth are the corresponding Zeeman contributions, and the last term corresponds to the interaction between the two-spin species. Due to the typical \(^{13}\text{C}^{13}\text{C}\) spatial separation in samples with natural \(^{13}\text{C}\) abundance, the first term corresponds to a very weak interaction, which we neglect.

The term involving \( V_{\text{int}} \) corresponds to the hyperfine couplings between electronic and nuclear spins. A direct flip-flop between a P1 spin and a \(^{13}\text{C}\) spin is not allowed due to the large energy mismatch \( \gamma_1 B \ll |\gamma_S B| \). Then, we are left with:

\[
\sum_{k} \sum_{m} V_{\text{int}}(I_k, S_m) \approx \sum_{k} \sum_{m} A_{zz}^{(m,k)} s_m^z I_k^z + A_{zx}^{(m,k)} s_m^x I_k^x \quad (A.2)
\]

Notice here that the second term (known as pseudo-secular) cannot be truncated since, in the case of interest, the hyperfine energies exceed the nuclear Zeeman energy. For future reference, Eq. (A.1) can be easily extended to include an NV center provided the magnetic field is chosen so that the frequency of the \(|0\rangle \leftrightarrow |-1\rangle\) NV transition matches the electron Larmor frequency, namely, when \(|\gamma_S B| \sim \Delta/2\), where \( \Delta = 2.87 \text{ GHz} \) denotes the NV zero field splitting. This condition — met near 51 mT — immediately implies that the transfer of polarization from carbons coupled to an NV center is field dependent.

### III. The four-spin system and the effective \(^{13}\text{C}^{13}\text{C}\) mechanisms

To analyze the dynamics induced by Eqns. (A.1) and (A.2), we start by considering a simple system with two \(^{13}\text{Cs}\) and two P1 centers, as shown in Fig. S2. Our objective is to derive an effective description of the dynamics of polarization within a spin system only composed by \(^{13}\text{Cs}\). We start by writing down the Hamiltonian \( H_T \) in Eq. (A.1) for the model depicted in Fig. S2,

\[
H_T = -\omega_S l_1^z - \omega_1 l_4^z + \omega_S s_2^z + \omega_S s_3^z + A_{zz}^{12} s_2^z l_1^z + A_{zz}^{13} s_3^z l_1^z + A_{zz}^{14} s_3^z l_4^z + J_d (s_2^x s_3^x + s_2^y s_3^y) \quad (A.3)
\]

Here, \( \omega_S = |\gamma_S B| \), \( \omega_1 = \gamma_1 B \) (note both frequencies are positive), and \( J_d \) is the dipolar coupling between the two P1 centers (spins 2 and 3 in Fig. S2), and, as stated above, we assume an energy-matching external magnetic field \( B = 51 \text{ mT} \). Since \( \omega_S \) is the leading energy scale in \( H_T \), we can split it into three blocks given by the subspaces

**Figure S2. The four-spin system.** Two \(^{13}\text{Cs}\) interact with two P1 centers. Each number labels the corresponding spin (see text) corresponding to P1-spin projection equal to 1, 0, -1. These blocks are not mixed by \( H_T \) since \([S_2^z + S_3^z, H_T] = 0\).
Furthermore, subspaces with spin projection 1 or -1 cannot yield an effective $^{13}$C-$^{13}$C interaction since the dynamics within these subspaces are equivalent to the evolution of the two $^{13}$Cs in the presence of an external static magnetic field. Thus, we restrict ourselves to the subspace of zero spin projection for the two PI spins.

By introducing the norm of the hyperfine interactions,

$$
\Delta_{12} = \sqrt{(A_{zz}^{12})^2 + (A_{xz}^{12})^2}
$$

(A.4)

$$
\Delta_{34} = \sqrt{(A_{zz}^{34})^2 + (A_{xz}^{34})^2}.
$$

(A.5)

we identify two different regimes defined by the hierarchy in the energy scales: Regime 1, where $\Delta_{12} \geq \Delta_{34} > J_d > \omega_1$, and Regime 2, where $J_d > \Delta_{12} \sim \Delta_{34}, \omega_1$.

In what follows we analyze both regimes in detail.

**Regime 1. Hyperfine-dominated limit**

This case is characterized by $\Delta_{12} \geq \Delta_{34} > J_d > \omega_1$. Since the $^{13}$C quantization axis is essentially given by the hyperfine vector, it is natural to rewrite $H_T$ as:

$$
H_T = -\omega_1 I_x^z - \omega_d I_x^4 + \omega_5 S_S^z + \omega_3 S_S^x + \Delta_{12}(S_S^z I_x^z + A_{zz}^{12}I_x^z) + S_Z^z(A_{zz}^{12}I_x^z + A_{xz}^{12}I_x^z) + J_d(S_S^z S_S^x + S_S^Y S_Y^Y)
$$

(A.6)

In order to diagonalize the hyperfine interaction, we rotate the local basis of each $^{13}$C spin to obtain

$$
H_T = -\omega_z^{(1)} \tilde{I}_z + \omega_x^{(1)} \tilde{I}_x - \omega_z^{(4)} \tilde{I}_z + \omega_x^{(4)} \tilde{I}_x + \omega_5 S_S^z + \omega_3 S_S^x + \Delta_{12} S_Z^z \tilde{I}_z + \Delta_{34} S_S^x \tilde{I}_x + J_d(S_S^z S_S^x + S_S^Y S_Y^Y)
$$

(A.7)

where

$$
\omega_z^{(1)} = \omega_1 \frac{A_{zz}^{12}}{\Delta_{12}}
$$

$$
\omega_x^{(1)} = \omega_1 \frac{A_{zz}^{12}}{\Delta_{12}}
$$

$$
\omega_z^{(4)} = \omega_1 \frac{A_{zz}^{34}}{\Delta_{34}}
$$

$$
\omega_x^{(4)} = \omega_1 \frac{A_{zz}^{34}}{\Delta_{34}}
$$

Now we explicitly write down the Hamiltonian $H_T$ in the subspace of interest. Only for the purposes of simplifying the notation, we assume $\omega_z^{(1)} = \omega_z^{(4)} = \omega$ (in our simulations below, however, we lift this restriction and consider these values not necessarily equal).

|          | $|\uparrow\uparrow\uparrow\downarrow\rangle$ | $|\uparrow\uparrow\downarrow\uparrow\rangle$ | $|\uparrow\downarrow\downarrow\uparrow\rangle$ | $|\downarrow\uparrow\downarrow\uparrow\rangle$ | $|\downarrow\uparrow\uparrow\downarrow\rangle$ | $|\uparrow\uparrow\uparrow\uparrow\rangle$ | $|\uparrow\uparrow\uparrow\down\rangle$ | $|\uparrow\up\down\rangle$ |
|----------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| $|\uparrow\uparrow\uparrow\down\rangle$ | $-\omega + \frac{\Delta_{12} - \Delta_{34}}{4}$ | $\frac{3d}{2}$ | $\omega_x^{(4)}/2$ | 0 | $\omega_z^{(1)}/2$ | 0 | 0 | 0 |
| $|\uparrow\uparrow\down\uparrow\rangle$ | $\frac{\Delta_{12} + \Delta_{34}}{4}$ | $\frac{3d}{2}$ | $-\omega + \frac{\Delta_{12} - \Delta_{34}}{4}$ | 0 | $\omega_x^{(4)}/2$ | 0 | $\omega_z^{(1)}/2$ | 0 |
| $|\uparrow\down\down\uparrow\rangle$ | $\omega_z^{(4)}/2$ | 0 | $\frac{\Delta_{12} + \Delta_{34}}{4}$ | $\frac{3d}{2}$ | 0 | 0 | $\omega_z^{(1)}/2$ | 0 |
| $|\down\up\down\uparrow\rangle$ | 0 | $\omega_z^{(4)}/2$ | $\frac{3d}{2}$ | $-\omega + \frac{\Delta_{12} - \Delta_{34}}{4}$ | 0 | 0 | 0 | $\omega_z^{(1)}/2$ |
| $|\down\up\up\down\rangle$ | $\omega_x^{(4)}/2$ | 0 | 0 | 0 | $\omega_z^{(1)}/2$ | $\frac{\Delta_{12} + \Delta_{34}}{4}$ | 0 | $\omega_z^{(1)}/2$ |
| $|\down\down\up\up\rangle$ | 0 | $\omega_x^{(4)}/2$ | 0 | 0 | $\frac{3d}{2}$ | $\frac{\Delta_{12} + \Delta_{34}}{4}$ | 0 | $\omega_z^{(1)}/2$ |
Here, the prime in the $^{13}$C spin states indicates the quantization axis defined by the hyperfine vector. The two states highlighted in yellow and the two in green are nearly degenerate. If we focus on the green pair, i.e. states $|\uparrow'\downarrow\uparrow\downarrow\rangle$ and $|\downarrow'\uparrow\downarrow\uparrow\rangle$ (same argument valid for the pair $|\uparrow'\downarrow\downarrow\uparrow\rangle$ and $|\downarrow'\uparrow\uparrow\downarrow\rangle$), second order perturbation theory yields a small energy difference $\delta$ that breaks the degeneracy,

$$ \delta^{[1]} \approx 2\omega_\chi^{(1)}\omega_\chi^{(4)}\omega \left| \frac{\Delta_{12} - \Delta_{34}^2}{\Delta_{12}\Delta_{34}} \right| $$

(A.9)

where the index 1 in square brackets stands for Regime 1. An effective description dealing only with $^{13}$C spins needs to incorporate a local field term accounting for this energy shift between the states $|\uparrow'\downarrow\rangle$ and $|\downarrow'\uparrow\rangle$.

Effective flip-flops can occur if we consider third-order processes,

$$ |\uparrow'\downarrow\uparrow\downarrow\rangle \rightarrow |\uparrow'\downarrow\uparrow\uparrow\rangle \rightarrow |\uparrow'\uparrow\downarrow\uparrow\rangle \rightarrow |\downarrow'\uparrow\downarrow\uparrow\rangle $$

and

$$ |\uparrow'\uparrow\downarrow\downarrow\rangle \rightarrow |\uparrow'\uparrow\downarrow\uparrow\rangle \rightarrow |\uparrow'\downarrow\downarrow\uparrow\rangle \rightarrow |\downarrow'\downarrow\uparrow\rangle $$

The sequences above include a single $^{13}$C spin-flip, a dipolar P1-P1 flip-flop, and finally a second single $^{13}$C spin flip. The entire process can be thought of as a virtual four-body interaction, already hinting at the effective mechanism of $^{13}$C-$^{13}$C flip-flop. More specifically, such a flip-flop occurs with a third-order coupling element

$$ j_{\text{eff}}^{[1]} \approx \frac{4\omega_\chi^{(1)}\omega_\chi^{(4)}J_d}{\Delta_{12}\Delta_{34}}. $$

(A.10)

Then, the proposed effective Hamiltonian describing the dynamics of the $^{13}$C pair in Regime 1 is:

$$ H_{\text{eff}}^{[1]} = -\frac{\delta^{[1]}}{2} I_x^2 + \frac{\delta^{[1]}}{2} I_y^2 + j_{\text{eff}}^{[1]} \left( I_x I_x + I_y I_y \right) $$

(A.11)

We compare the dynamics induced by $H_T$ (Eq. (A.7)) and by $H_{\text{eff}}^{[1]}$ (Eq. (A.11)) in Fig. S3. In particular, we consider an initial state given by $|\uparrow'\downarrow\uparrow\rangle$ and monitor the time evolution of the polarization for both $^{13}$Cs. The comparison shows that the effective flip-flop mechanism can have a strength of up to a few kHz for strongly coupled P1 pairs. In fact, the flip-flop dynamics is dominant when $\delta^{[1]} < j_{\text{eff}}^{[1]} \propto J_d$. Conversely, if the P1-P1 interaction is weak, then $\delta^{[1]} > j_{\text{eff}}^{[1]}$, and correspondingly the polarization remains localized. It is therefore natural to envision a direct generalization of $H_{\text{eff}}^{[1]}$ into the Anderson localization problem [9] for a large set of $N_t$ spins. In such case, the P1-P1 interaction controls the dynamical phase of the $^{13}$C system. In our simple two-spin case, a symbolic estimate for this localized-to-delocalized transition would occur at a critical interaction ($\delta^{[1]} \approx j_{\text{eff}}^{[1]}$)

$$ J_d^c \approx \omega \left| \frac{\Delta_{12} - \Delta_{34}^2}{2\Delta_{12}\Delta_{34}} \right|. $$

(A.12)

We stress that an estimate of the mean P1-P1 interaction (or, equivalently, P1 concentration) needed to ensure spin diffusion within the $^{13}$C system requires a good knowledge of the statistical distribution of hyperfine couplings.
We caution that the denominator in $J_{\text{eff}}$ (Eq. (A.10)) cannot be arbitrarily small. Further, the effective description also fails if there is a large mismatch between the hyperfine couplings (for example, when $\Delta_{12} \gg \Delta_{34} \sim \omega$). In such a case, the dynamics is essentially given by an uncorrelated single-spin flip at a frequency given by $\omega^{(4)}_x$,

\begin{align*}
|\uparrow\downarrow\uparrow\downarrow'\rangle &\leftrightarrow |\uparrow'\downarrow\uparrow\downarrow'\rangle \\
|\downarrow\uparrow\uparrow\downarrow'\rangle &\leftrightarrow |\downarrow\uparrow\uparrow\downarrow'\rangle \\
|\uparrow'\downarrow\downarrow\uparrow'\rangle &\leftrightarrow |\uparrow\downarrow\uparrow\uparrow'\rangle \\
|\downarrow'\uparrow\up\uparrow\down\rangle &\leftrightarrow |\down\up\up\down\rangle
\end{align*}

and no polarization transfer happens (an equivalent example can be given for $\Delta_{34} \gg \Delta_{12} \sim \omega$). This scenario implies that strongly hyperfine-coupled $^{13}$Cs cannot transfer the polarization directly to bulk $^{13}$Cs. Nevertheless, strongly coupled $^{13}$Cs can effectively interact with ‘moderately’ hyperfine-coupled $^{13}$Cs, and these, in turn, interact with more weakly-hyperfine-coupled $^{13}$Cs, thus allowing the polarization to gradually cascade down to the bulk carbons.

Finally, by inspection of the matrix representation of $H_T$ in (A.8), it would be natural to expect terms of the form $I_i^z I_j^z$ in $H_{\text{eff}}^{[1]}$. These terms should account for the energy difference between the subspace spanned by $\{|\uparrow'\downarrow\rangle, |\downarrow\up\rangle\}$ and the subspace spanned by $\{|\up\up\rangle, |\down\down\rangle\}$. However, the simplified model employed herein is only useful to analyze the effective flip-flop mechanism and a more detailed analysis is required to derive the effective coupling element corresponding to an Ising term of the form $I_i^z I_j^z$. Such an approach, at the same time, would extend our previous discussion on (Anderson-) localization-delocalization into the many-body localization-delocalization problem.

**Figure S3.** Comparison of the flip-flop dynamics (polarization transport) between the Hamiltonians $H_T$ (a and c) and $H_{\text{eff}}^{[1]}$ (b and d). In all the cases, $A_{12}^{z\Phi} = A_{12}^{z\Pi} = 40$ MHz, $A_{34}^{z\Phi} = A_{34}^{z\Pi} = 9$ MHz and the initial state is $|\uparrow\downarrow\uparrow\downarrow'\rangle$. In (a) and (b), $J_d = 1$ MHz. In (c) and (d), $J_d = 5$ MHz.
Regime 2. Dipolar-dominated limit

This regime is characterized by \( J_d > \Delta_{12} \approx \Delta_{34}, \omega_1 \), which means that the dipolar \( P1-P1 \) interaction defines the leading energy scale. We first consider the case \( J_d > \Delta_{12} \approx \Delta_{34} \gtrsim \omega_1 \); notice, however, that since \( J_d \) does not largely exceed \( \sim 1 \) MHz for moderate \( P1 \) concentrations (50 ppm in the present case), both hyperfine interactions would have strengths comparable to \( \omega_1 \) (or, at least, not much higher than \( \omega_1 \)), effectively limiting this regime to a narrow window. Then, we can choose here the \(^{13}\)C quantization axis to be given by the Zeeman interaction with the external magnetic field.

We further simplify this regime and assume, for now, \( A_{2z}^{12} = A_{2z}^{34} = 0 \). Then, the matrix representation of \( H_T \) in Eq. (A.3) for the subspace of interest is

\[
\begin{array}{cccccccc}
\langle \uparrow \downarrow \uparrow \rangle & | \uparrow \downarrow \uparrow \rangle & | \uparrow \downarrow \downarrow \rangle & | \downarrow \uparrow \uparrow \rangle & | \downarrow \downarrow \uparrow \rangle & | \downarrow \downarrow \downarrow \rangle & | \downarrow \uparrow \downarrow \rangle & | \downarrow \uparrow \downarrow \rangle \\
\langle \uparrow \uparrow \uparrow \rangle & -\omega_1 & 0 & 0 & 0 & 0 & 0 & 0 \\
\langle \uparrow \uparrow \uparrow \rangle & J_d/2 & -\omega_1 & 0 & 0 & 0 & 0 & 0 \\
\langle \uparrow \uparrow \downarrow \rangle & -A_{2x}^{34}/4 & 0 & 0 & 0 & 0 & 0 & 0 \\
\langle \uparrow \downarrow \uparrow \rangle & 0 & A_{2z}^{34}/4 & J_d/2 & 0 & 0 & 0 & 0 \\
\langle \uparrow \downarrow \downarrow \rangle & 0 & 0 & 0 & -\omega_1 & J_d/2 & 0 & 0 \\
\langle \downarrow \uparrow \uparrow \rangle & 0 & 0 & 0 & 0 & 0 & -A_{2x}^{12}/4 & 0 \\
\langle \downarrow \downarrow \uparrow \rangle & 0 & 0 & 0 & 0 & 0 & 0 & -A_{2x}^{12}/4 \\
\langle \downarrow \downarrow \downarrow \rangle & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{array}
\]

Now we transform the Hamiltonian into a basis that diagonalizes the dipolar \( P1-P1 \) interaction \( J_d(S_z^2 S_z^3 + S_z^3 S_z^z) \). Here, the eigenstates are

\[
|+\rangle = \frac{1}{\sqrt{2}}(|\uparrow \downarrow \rangle + |\downarrow \uparrow \rangle) \quad (A.14)
\]

\[
|\rangle = \frac{1}{\sqrt{2}}(|\uparrow \downarrow \rangle - |\downarrow \uparrow \rangle) \quad (A.15)
\]

Then, the Hamiltonian matrix is given by

\[
\begin{array}{cccccccc}
\langle \uparrow \downarrow \rangle & | \uparrow \uparrow \rangle & | \uparrow \downarrow \rangle & | \downarrow \uparrow \rangle & | \downarrow \downarrow \rangle & | \downarrow \uparrow \rangle & | \downarrow \downarrow \rangle & | \downarrow \uparrow \rangle \\
\langle \uparrow \uparrow \rangle & -\omega_1 - J_d/2 & 0 & 0 & 0 & 0 & 0 & 0 \\
\langle \uparrow \downarrow \rangle & 0 & -\omega_1 + J_d/2 & -A_{2x}^{34}/4 & 0 & 0 & 0 & 0 \\
\langle \downarrow \uparrow \rangle & 0 & -A_{2z}^{34}/4 & -J_d/2 & 0 & 0 & 0 & 0 \\
\langle \downarrow \downarrow \rangle & 0 & 0 & 0 & -\omega_1 & J_d/2 & 0 & 0 \\
\langle \uparrow \downarrow \rangle & 0 & 0 & 0 & 0 & 0 & -A_{2x}^{12}/4 & 0 \\
\langle \downarrow \uparrow \rangle & 0 & 0 & 0 & 0 & 0 & 0 & -A_{2x}^{12}/4 \\
\langle \downarrow \downarrow \rangle & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\langle \downarrow \uparrow \rangle & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{array}
\]

The subspace highlighted in green contains two pairs of quasi-degenerate states: \(|\uparrow \downarrow \rangle\) and \(|\downarrow \uparrow \rangle\) with energy \(-J_d/2\), and \(|\uparrow \uparrow \rangle\) and \(|\downarrow \uparrow \rangle\) with energy \(+J_d/2\). As before, second order perturbation theory provides an estimate for the energy shift that breaks degeneracy,

\[
\delta^{(2)} \approx \omega_1 \frac{|(A_{2z}^{34})^2 - (A_{2x}^{12})^2|}{8J_d^2} \quad (A.17)
\]
where the index 2 in square brackets refers to Regime 2. Again, an effective description only dealing with $^{13}$C spins needs to incorporate a local field term accounting for $\delta^{[2]}$.

An effective flip-flop mechanism can be derived also from second order processes,

$$
|\uparrow + \downarrow\rangle \rightarrow |\uparrow - \uparrow\rangle \rightarrow |\downarrow + \uparrow\rangle
$$

and

$$
|\uparrow - \downarrow\rangle \rightarrow |\uparrow + \downarrow\rangle \rightarrow |\downarrow - \downarrow\rangle
$$

This type of transition involves a sequence of two $^{13}$C spin flips mediated by a virtual change in the P1 interaction energy. The obtained effective flip-flop mechanism has a coupling element

$$
J_{\text{eff}}^{[2]} \approx \frac{A_{2x}^{34} A_{2x}^{12}}{4T_d}, \quad (A.18)
$$

where we use $J_d > \omega_1$ to drop the dependence of $\omega_1$ in the denominator. This leads us to propose the following effective Hamiltonian,

$$
H_{\text{eff}}^{[2]} = -\frac{\delta^{[2]}_1}{2} I_1^z + \frac{\delta^{[2]}_4}{2} I_4^z + J_{\text{eff}}^{[2]} (I_1^z I_4^z + I_1^y I_4^y), \quad (A.19)
$$

From Eqns. (A.17) and (A.18), it is straightforward to verify that

$$
\delta^{[2]} \lesssim \frac{\omega_1}{J_d} J_{\text{eff}}^{[2]} < J_{\text{eff}}^{[2]}, \quad (A.20)
$$

thus the polarization dynamics in Regime 2 is always delocalized.

We illustrate the accuracy of $H_{\text{eff}}^{[2]}$ by comparing the polarization dynamics induced by Eqns. (A.3) and (A.19). In Fig. S4 we consider an initial state given by $|\uparrow \downarrow \downarrow \rangle$ and monitor the time evolution of the polarization for both $^{13}$Cs using the complete Hamiltonian $H_T$ and the effective $H_{\text{eff}}^{[2]}$. The comparison shows that the effective flip-flop mechanism can have a strength of hundreds of kHz, though only within the narrow window where $J_d \sim A_{2x}^{12} \sim A_{2x}^{34} \gtrsim \omega_1$. Beyond this condition (i.e., when $J_d \approx \omega_1$) we expect the effective Hamiltonian to gradually deviate from the exact $H_T$, since in Eq. (A.18) we disregard the effect of $\omega_1$ in the denominator of the coupling parameter. This situation is seen in Fig. S4(a) (where $J_d = A_{2x}^{12} = 1$ MHz, $A_{2x}^{34} = 750$ kHz, and $\omega_1 = \gamma_1 B \approx 500$ kHz). The modulations present in the dynamics of the effective flip-flop Hamiltonian $H_{\text{eff}}^{[2]}$ can be more important if $A_{3x}^{12}, A_{3x}^{34} \neq 0$ because these terms contribute to the diagonal Hamiltonian matrix elements. Note that as long as $J_d$ remains the leading energy scale, Eq. (A.18) applies beyond the condition $J_d > \Delta_{12} \sim \Delta_{34} \gtrsim \omega_1$ to include the limit where the hyperfine shifts go to zero, i.e. $J_d > \omega_1 > \Delta_{12} \sim \Delta_{34}$.

A complete hierarchical picture of the $^{13}$C-$^{13}$C interactions can thus be drawn: Medium strength (few kHz) effective interactions develop inside the classical “diffusion barrier”, provided the frequency mismatch between hyperfine couplings is sufficiently small (Regime 1); stronger effective interactions (reaching up to 100 kHz) become possible as carbons occupy positions farther removed from the electron spins, to subsequently decay as the hyperfine couplings gradually vanish (Regime 2). In this latter limit, carbon couplings take the value corresponding to that defined by the dipolar spin coupling between bulk nuclei.

IV. The effect of RF excitation
To study the impact of RF on the system dynamics, we go back to the four-spin model and rewrite the Hamiltonian in Eq. (A.6) as,

\[
H_T = -\omega_1 I_1^z - \omega_1 I_4^x + \omega_5 S_2^z + \omega_7 S_3^z + S_2^z (A_{12}^{12} I_1^z + A_{12}^{12} I_4^x) + S_3^z (A_{34}^{34} I_4^z + A_{34}^{34} I_4^x) + I_d \left( S_2^x S_3^x + S_2^y S_3^y \right) + (I_1^x + I_4^x) \Omega \cos(\omega_r t) \tag{A.21}
\]

Now, assuming for concreteness Regime 1 and transforming into the hyperfine basis, we obtain

\[
H_T = -\omega_z (1) I_1^z - \omega_x (1) I_1^x - \omega_z (4) I_4^z + \omega_x (4) I_4^x + \omega_5 S_2^z + \omega_7 S_3^z + \Delta_{12} S_2^z I_1^z + \Delta_{34} S_3^z I_4^z + I_d \left( S_2^x S_3^x + S_2^y S_3^y \right) + \left( \Omega_z^{(1)} I_1^z + \Omega_x^{(1)} I_1^x \right) \cos(\omega_r t) + \left( \Omega_z^{(4)} I_4^z + \Omega_x^{(4)} I_4^x \right) \cos(\omega_r t) \tag{A.22}
\]

where

\[
\begin{align*}
\Omega_z^{(1)} &= \Omega \frac{A_{12}^{12}}{\Delta_{12}} \\
\Omega_x^{(1)} &= \Omega \frac{A_{12}^{12}}{\Delta_{12}} \\
\Omega_z^{(4)} &= \Omega \frac{A_{34}^{34}}{\Delta_{34}} \\
\Omega_x^{(4)} &= \Omega \frac{A_{34}^{34}}{\Delta_{34}}
\end{align*}
\]
In the rotating frame, after performing standard time averaging, we finally write

\[ H_T = \left( -\omega_z^{(1)} + \Omega_z^{(1)} - \omega_{\text{rf}} \right) \vec{I}_1^z + \Delta_{12} S_z^2 \vec{I}_1^z + \left( -\omega_z^{(4)} + \Omega_z^{(4)} - \omega_{\text{rf}} \right) \vec{I}_4^z + \Delta_{34} S_z^2 \vec{I}_4^z \\
+ \Omega_x^{(1)} \vec{I}_1^x + \Omega_x^{(4)} \vec{I}_4^x + \omega_5 S_z^2 + \omega_5 S_z^2 + J_d \left( S_z^x S_z^x + S_z^y S_z^y \right) \]

To highlight the ‘hybrid’ electron/nuclear-spin nature of the transitions, here we assume both \( ^{13}\text{C} \) are polarized and the P1 pair is in the subspace of zero spin projection (note that this is in contrast with the case in the main text where we assume both P1s are unpolarized). Fig. S5(a-b) shows both the nuclear and electronic polarization as a function of the excitation frequency \( \omega_{\text{rf}} \) and the P1-P1 coupling parameter \( J_d \). To help understand these results, Figure S5(c) shows the energy spectrum as a function of \( J_d \) with an identification of the eigenstates in the two extreme cases \( J_d = 0 \) (left) and \( J_d \sim 5 \text{ MHz} \) (right). In the limit of \( J_d = 0 \), four possible transitions can be identified, which correspond to each \( ^{13}\text{C} \) flipping independently. As \( J_d \) increases, the resonance frequencies are shifted and the states involved in each transition change accordingly. As the eigenstates feature contributions from different electron and nuclear spin projections, all transitions in this regime involve simultaneous nuclear and electronic spin-flips.

Figure S5. Dynamical response in the presence of RF excitation. (a) Polarization of \( ^{13}\text{C} \) spins as a function of the P1-P1 dipolar interaction \( J_d \) and RF excitation \( \omega_{\text{rf}} \). Both carbon spins are initially polarized. (b) P1 polarization (initially assumed to be zero) as a function of \( J_d \) and \( \omega_{\text{rf}} \). (c) Eigenenergies as a function of \( J_d \) in the subspace of zero spin projection for the P1 spins. The same resonance frequencies shown in (a,b) are shown here with arrows. For the eigenstates in the regime of large P1-P1 interaction (e.g., \( J_d \sim 5 \text{ MHz} \)), the coefficients verify \( c_1 \approx c_2 \) and \( d_1 \gg d_2 \). In all cases we assume \( A_{12}^{zz} = A_{12}^{xx} = 14 \text{ MHz} \), \( A_{34}^{zz} = A_{34}^{xx} = 9 \text{ MHz} \), \( B = 51 \text{ mT} \). For (a) and (b), \( \Omega = 75 \text{ kHz} \).

In the rotating frame, after performing standard time averaging, we finally write

\[ H_T = \left( -\omega_z^{(1)} + \Omega_z^{(1)} - \omega_{\text{rf}} \right) \vec{I}_1^z + \Delta_{12} S_z^2 \vec{I}_1^z + \left( -\omega_z^{(4)} + \Omega_z^{(4)} - \omega_{\text{rf}} \right) \vec{I}_4^z + \Delta_{34} S_z^2 \vec{I}_4^z \\
+ \Omega_x^{(1)} \vec{I}_1^x + \Omega_x^{(4)} \vec{I}_4^x + \omega_5 S_z^2 + \omega_5 S_z^2 + J_d \left( S_z^x S_z^x + S_z^y S_z^y \right) \]

To highlight the ‘hybrid’ electron/nuclear-spin nature of the transitions, here we assume both \( ^{13}\text{C} \) are polarized and the P1 pair is in the subspace of zero spin projection (note that this is in contrast with the case in the main text where we assume both P1s are unpolarized). Fig. S5(a-b) shows both the nuclear and electronic polarization as a function of the excitation frequency \( \omega_{\text{rf}} \) and the P1-P1 coupling parameter \( J_d \). To help understand these results, Figure S5(c) shows the energy spectrum as a function of \( J_d \) with an identification of the eigenstates in the two extreme cases \( J_d = 0 \) (left) and \( J_d \sim 5 \text{ MHz} \) (right). In the limit of \( J_d = 0 \), four possible transitions can be identified, which correspond to each \( ^{13}\text{C} \) flipping independently. As \( J_d \) increases, the resonance frequencies are shifted and the states involved in each transition change accordingly. As the eigenstates feature contributions from different electron and nuclear spin projections, all transitions in this regime involve simultaneous nuclear and electronic spin-flips.

V. Master equation approach: Spectral chain

This section of the Supplementary Material expands on the results of Fig. 4B in the main text, namely the response
of the $^{13}$C NMR signal upon application of a train of RF pulse of variable separation simultaneous with optical illumination. Experimental results at various excitation frequencies along their inverse Laplace transforms are presented in Fig. S6. While a full quantum mechanical model is impractical, we can employ a classical master equation approach to analyze the magnetization flow from strongly hyperfine-coupled $^{13}$Cs to bulk $^{13}$Cs. The physical picture is based on a one-dimensional chain, where each link can be viewed as a spin set with a specific spectral location (hyperfine shift), as shown in Fig. 4C of the main text. More precisely, the magnetization charge $\{q_i\}_{i=1}^m$ of each of these boxes is described by

$$ \frac{d}{dt} q_1 = -\gamma_{12}q_1 + \gamma_{21}q_2 - \beta_1 q_1 $$  \hspace{1cm} (A.24)

$$ \frac{d}{dt} q_2 = -\gamma_{21}q_2 - \gamma_{23}q_2 + \gamma_{12}q_1 + \gamma_{32}q_3 - \beta_2 q_2 $$  \hspace{1cm} (A.25)

$$ \frac{d}{dt} q_3 = -\gamma_{32}q_3 - \gamma_{34}q_3 + \gamma_{23}q_2 + \gamma_{43}q_4 - \beta_3 q_3 $$  \hspace{1cm} (A.26)

$$ \vdots $$

$$ \frac{d}{dt} q_k = -\gamma_{k,k-1}q_k - \gamma_{k,k+1}q_k + \gamma_{k-1,k}q_{k-1} + \gamma_{k+1,k}q_{k+1} - \beta_k q_k - a_{RF}g(t) q_k $$ \hspace{1cm} (A.27)

$$ \vdots $$

$$ \frac{d}{dt} q_m = \gamma_{m-1,m}q_{m-1} - \beta_m q_m $$ \hspace{1cm} (A.28)

Here, $\gamma_{ij}$ stands for the transfer rate from box $i$ to box $j$, and $\beta_i$ represents the loss of magnetization due to nuclear spin-lattice relaxation. The RF excitation is resonant with box $k$, $g(t)$ stands for the shape of the train of RF pulses, and $a_{RF}$ is the amplitude of each pulse (here seen to act as a polarization sink). Consistent with the relative spectral proximity required for electron-spin-mediated transport (see Eqs. (A.10) and (A.12)), we only consider interactions between immediate spectral neighbors (i.e., $k-1$ and $k+1$) though additional contributions from farther removed boxes can be easily incorporated. Further, we neglect any backflow from the last box to the rest of the chain, and ignore non-linear (i.e., ‘blockade’) effects arising from saturation of the magnetization in a given box; this latter regime can always be attained when the illumination power is sufficiently low. The set of equations can then be written in the standard matrix form

$$ \frac{d}{dt} Q = AQ, $$ \hspace{1cm} (A.29)

with

$$ A = \begin{pmatrix}
-\gamma_{12} - \beta_1 & \gamma_{21} & 0 & 0 & \ldots & \ldots & 0 \\
\gamma_{12} & -\gamma_{21} - \gamma_{23} - \beta_2 & \gamma_{32} & 0 & 0 & 0 & 0 \\
0 & \gamma_{23} & \ldots & \gamma_{k-1,k} & 0 & 0 & 0 \\
0 & 0 & \ldots & \gamma_{k-1,k} - \gamma_{k,k+1} - \beta_k - a_{RF}g(t) & \gamma_{k+1,k} & 0 & 0 \\
0 & 0 & 0 & \gamma_{k+1,k} & \ldots & \ldots & \ldots \\
0 & 0 & 0 & 0 & \ldots & \ldots & 0 \\
0 & 0 & 0 & 0 & \ldots & 0 & \gamma_{m-1,m} - \beta_m
\end{pmatrix}. $$
It is natural to split the evolution into intervals with and without RF excitation, since these correspond to $A_1 \equiv A(g = 1)$ and $A_0 \equiv A(g = 0)$, respectively. Using $\tau$ to denote the inter-pulse delay and $\tau_{RF}$ to indicate the RF pulse duration (here fixed to 1ms), the evolution of the magnetizations in each composite interval is given by

$$Q(\tau + \tau_{RF}) = \exp(A_0 \tau) \exp(A_1 \tau_{RF}) Q_0.$$  \hspace{1cm} (A.30)
Given a total evolution time $T$, the number of composite intervals is given by $n_p = T / (\tau + \tau_{RF})$. Then, the final magnetization is given by

$$Q(T) = [\exp(A_0 \tau) \exp(A_{RF} \tau)]^{n_p} Q_0.$$  \hfill (A.31)

In our simulations, we consider an initial condition given by $q_1 = 1$ and $q_i = 0 \; \forall i > 1$. This is a crude approximation since we do not include the continuous effect of the optical pumping. Additionally, we also assume for simplicity $\beta_i = 0 \; \forall i$. The intensity of the RF irradiation is the leading scale of the problem, here assumed to be $a_{RF} = 1 \text{ MHz}$. The total time considered is always $T = 1 \text{ s}$.

The first case we study corresponds to a uniform set of coupling constants, $\gamma_{ij} = \gamma_{ji} = \gamma_0$. Figure S7 shows the normalized magnetization charge in the last box after the full evolution $q_m(T = 1 \text{ s})$ as a function of the interpulse delay time $\tau$, for different $\gamma_0$. The system has $m = 40$ boxes and the RF-irradiated box is always $k = 20$.

Figure S7. Normalized magnetization in the end box ($m\text{-th}$) in a system of 40 boxes upon RF irradiation in box $k = 20$. The couplings constants are uniformly distributed, $\gamma_{ij} = \gamma_{ji} = \gamma_0$, with $\gamma_0$ given in the inset. The solid lines are given by stretched-exponential fittings, with $\varepsilon = 1$ for the blue and green cases, and $\varepsilon = 0.8$ for the red case.

In Fig. S8 we investigate the dependence of $q_m(T = 1 \text{ s})$ on the point of RF excitation across the chain. In the case of uniform couplings (Fig. S8a), we verify that the observed time-scale does not depend on the location of the saturated box. In Fig. S8b we consider a small, localized fraction of the chain has much stronger couplings than the rest. In particular, we assume the coupling set given by

$$\gamma_{i,i+1} = \gamma_{i+1,i} = \gamma_0 + 100\gamma_0 \exp \left\{ -\left( \frac{k_0 - i}{K_0} \right)^2 \right\},$$  \hfill (A.32)

where we choose $k_0 = 15$ and $K_0 = 2$. In this case, we observe a stronger attenuation of $q_m(T = 1 \text{ s})$ as we irradiate the boxes close to the box $k_0$. This means that saturating strongly connected nodes produces a stronger degradation in the magnetization reaching the end of the chain.
**Figure S8.** Normalized magnetization in the end box of a chain of 40 upon RF irradiation. Lower panels explicitly show when boxes 15 and 25 are being (independently) irradiated (dashed lines are stretched exponential fittings, with $\varepsilon = 0.8$. In case (a), the couplings constants are uniformly distributed, $\gamma_{ij} = \gamma_{ji} = \gamma_0$, with $\gamma_0 = 1$ kHz. In (b) we consider a uniform distribution perturbed in a small region around $k_0 = 15$ where the couplings $\gamma_{i,i+1}$ can be up to 100 times $\gamma_0$. 