Supplementary Information:
Room-temperature cavity quantum electrodynamics with strongly-coupled Dicke states

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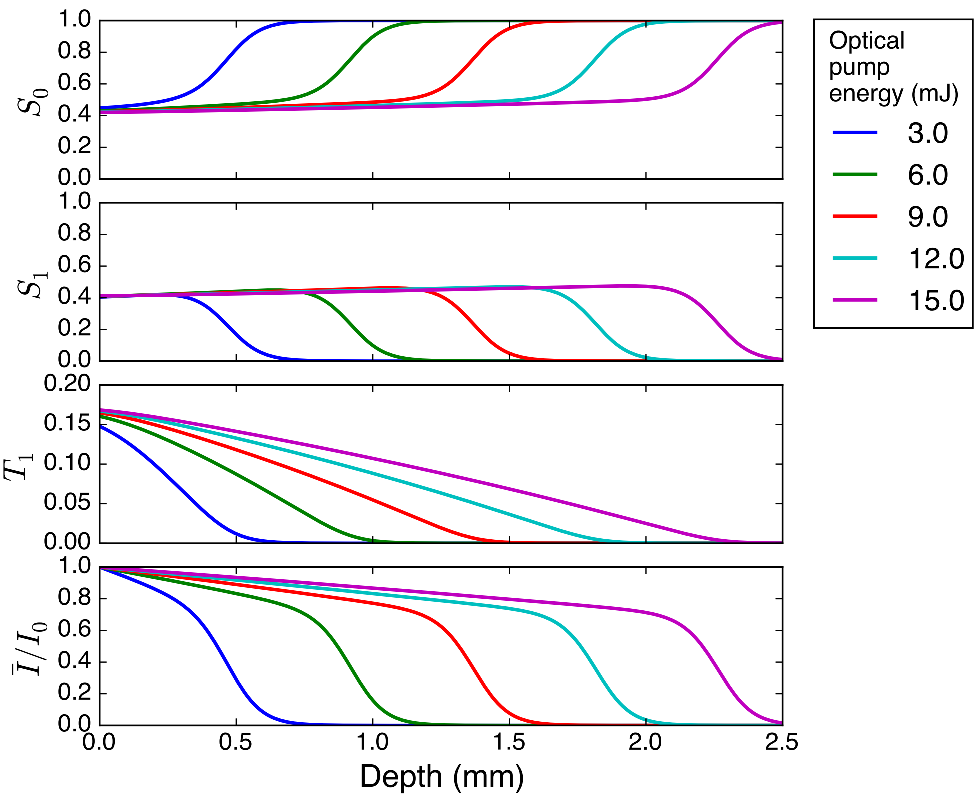
Penetration of optical pulses into pentacene:p-terphenyl crystal

Modelling the penetration of nanosecond optical pulses into a slab of pentacene-doped p-terphenyl followed the procedure outlined by Takeda [1], implementing a finite-difference time-domain technique to solve a coupled system of rate equations for the singlet and triplet state densities as a function of depth and a spatial differential equation for the optical beam irradiance. The optical parametric oscillator (OPO) used in this study emitted pulses of duration 5.5 ns at a wavelength of 592 nm with a (gaussian profile) spot diameter of 4 mm. The profile densities of the ground-state singlet, excited-state singlet, triplet state and the normalized optical pump irradiance for increasing optical pulse energies are shown in Fig. 1. For a pulse energy of 15 mJ, a penetration depth of ~ 2.5 mm was calculated for a 0.053% pentacene doped sample. The pentacene concentration places a limit on the thickness (and size) of the pentacene:p-terphenyl crystal given the available means of optical pumping. For our OPO with maximum pulse energy of 15 mJ, a cylindrical crystal with diameter 3 mm is sufficient for $\sim 10\%$ of the pentacene molecules to be excited into the triplet state, yielding an inversion of $\sim 10^{15}$ between the $|X\rangle$ and $|Z\rangle$ sub-levels. Importantly, for a crystal with given pentacene dopant concentration of a prescribed thickness, the triplet yield is a linear function of the laser energy when the penetration depth is less than crystal thickness. Although the number of triplets excited is crudely estimated, the linearity allows the $\sqrt{N}$ dependence of the ensemble spin-photon coupling g_{e} to be inferred by varying the OPO pulse energy. Furthermore, the linearity permits a comparison of estimates of the number of participating spins N from the numerical modelling and those extracted from the observed normal mode splitting.

Cavity design

To optimize a cavity for strong-coupling, the 'cooperativity' $C = g_{\mathrm{e}}^2/\kappa_{\mathrm{s}}\kappa_{\mathrm{c}}$ is a good figure of merit, yet by no means the criterion for strong-coupling, which is $g_{\mathrm{e}} \gg \kappa_{\mathrm{c}}, \kappa_{\mathrm{s}}$, where g_{e} is the ensemble spin-photon coupling, κ_{s} and κ_{c} are the decay rates for the spin and cavity modes respectively. The ensemble spin-photon coupling g_{e} for N spins situated at the magnetic field maximum is given by $g_{\mathrm{e}} = g_{\mathrm{s}}\sqrt{N} = \gamma\sqrt{\mu_0\hbar\omega_{\mathrm{c}}N/2V_{\mathrm{m}}}$, where μ_0 is the permeability of free-space, $\hbar$ is the reduced Planck constant, ω_{c} is the resonant frequency



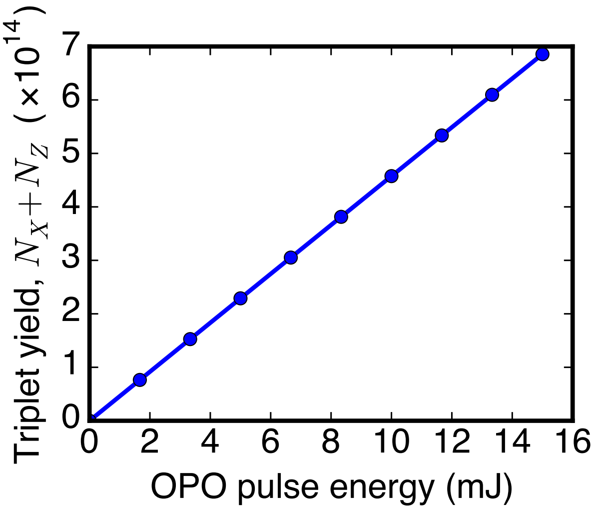
Supplementary Figure 1. State density and normalized irradiance depth profiles for pulses with increasing energies. Optical pulses have duration 5.5 ns and energies in the range 3-15 mJ. Graphs are (from top to bottom) ground singlet state S_0 density, excited singlet state S_1 density, spin-triplet state T_1 density, normalized optical pulse irradiance $\bar{I}/I_0$. The pentacene concentration is 0.053%. The penetration depth increases linearly as a function of optical pump pulse energy.

of the cavity and V_m is the magnetic mode volume. The magnetic mode volume, V_m is calculated as the ratio of the stored magnetic energy within the cavity, $\frac{1}{2}\mu_0 \int_\mathrm{V} |\mathbf{H}(\mathbf{r})|^2 dV$ to the maximum magnetic field energy density, $\frac{1}{2}\mu_0|\mathbf{H}(\mathbf{r})|^2$. Factoring out parameters that are independent of the cavity, like the number of spins N and the spin decoherence rate κ_s, reduces the 'cavity cooperativity' to

$$C_\mathrm{cav} \propto \frac{g_\mathrm{s}^2}{\kappa_\mathrm{c}} \propto \frac{\omega_\mathrm{c}}{\kappa_\mathrm{c} V_\mathrm{m}} \propto \frac{Q}{V_\mathrm{m}},$$

which is proportional to the Purcell factor [2] for a given frequency ω_c:

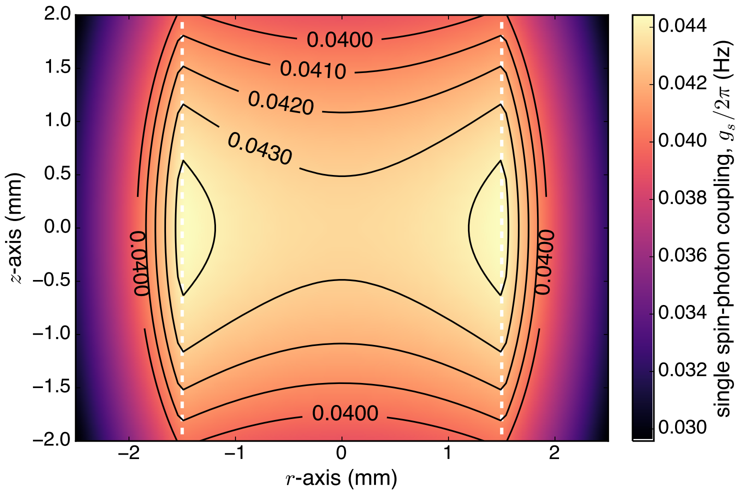
$$F_\mathrm{m} = \frac{2\pi c^3}{\omega_\mathrm{c}^3} \cdot \frac{Q}{V_\mathrm{m}}.$$



Supplementary Figure 2. Spin-triplet yield as a function of optical pump pulse energy. A pentacene-doped *p*-terphenyl crystal of thickness 3 mm and pentacene concentration 0.053% is excited by optical pump pulses of duration 5.5 ns and increasing energy. The OPO spot size diameter 4 mm.

Optimizing the Purcell factor is therefore a sound strategy for maximising the degree of strong-coupling. The cavity was modelled using a quasi-analytical radial mode-matching technique [3]. A hollow cylinder of single-crystal strontium titanate ($SrTiO_3$, STO) with outer diameter 10 mm, inner diameter 3 mm and height 11 mm was placed upon a cylindrical single-crystal sapphire (Al_2O_3) support (diameter 10 mm, height 6 mm). The dielectric stack was placed upon the floor of a cylindrical oxygen-free copper cavity with fixed diameter of 36 mm and a mechanically adjustable height of 18-24 mm. The pentacene *p*-terphenyl was housed inside the STO cylinder. The relative permittivity of STO at room temperature is $\varepsilon_{\mathrm{r}} = 318$ and that of sapphire is $\varepsilon_{\mathrm{r}} = 9.3$. The unloaded Q-factor is the reciprocal of the sum of the losses within the cavity, such as ohmic losses in cavity walls and dielectric losses within the dielectric resonator. The pentacene-doped *p*-terphenyl gain medium has low dielectric loss and low electric filling factor so its contribution to losses is negligible. The STO and sapphire had loss tangents of 9×10^{-5} and 2×10^{-6} at 1.45 GHz respectively. The surface resistance of the copper shield was 10 mΩ. The fundamental $\mathrm{TE}_{01\delta}$ mode had a frequency of $\approx$1.45 GHz, an unloaded Q-factor of 10,200 and a magnetic mode volume V_{m} of 0.25 cm^3.

The magnetic field $\mathbf{H}(\mathbf{r})$ within the cavity can be directly mapped onto to the coupling strength for an individual spin to a vacuum cavity photon, $g_{rms}(\mathbf{r}) = \mu_0 \gamma H(\mathbf{r})_{\text{vac}}$, where γ is the electron gyromagnetic ratio, μ_0 is the permeability of free-space and the vacuum magnetic field in the cavity is given by $H(\mathbf{r})_{\text{vac}} = \sqrt{\hbar\omega_{\text{c}}/2\mu_0 \int_{\text{V}} |\mathbf{H}(\mathbf{r})|^2 dV} \cdot |\mathbf{H}(\mathbf{r})|$. The single spin-photon coupling strength is shown in Fig. **3** for the region of the pentacene p-terphenyl illuminated by the optical pulse. Over the central portion $|r| < 1.5$ mm, $|z| < 2$ mm, the spin-photon coupling is $g_{\text{s}}/2\pi = 0.042 \pm 0.002$ Hz.



Supplementary Figure 3. **Single spin-photon coupling strength distribution within pentacene-doped medium.** The spin-photon coupling g_{s} for a single spin throughout the portion of the pentacene:p-terphenyl crystal illuminated by the optical pump pulse. Over the central portion $|r| < 1.5$ mm, $|z| < 2$ mm, the spin-photon coupling is $g_{\text{s}}/2\pi = 0.042 \pm 0.002$ Hz.

Master equations: decoherence and thermal noise

The time derivative of the expectation value of an operator $\hat{\mathcal{O}}$ can be written [4]:

$$\frac{d}{dt}\left\langle \hat{\mathcal{O}} \right\rangle = \text{tr}\left(\mathcal{O}\dot{\rho}\right) \tag{1}$$

where H is the Tavis-Cummings Hamiltonian:

$$H = \hbar\omega_{\text{c}} a^\dagger a + \frac{1}{2}\hbar\omega_{\text{s}} \sum_j^N \sigma_j^z + \hbar g_{\text{s}} \sum_j^N \left(\sigma_j^+ a + a^\dagger \sigma_j^-\right), \tag{2}$$

and ρ is the reduced spin-photon density matrix, given by $\dot{\rho} = (i\hbar)^{-1}[H,\rho] + \mathcal{L}[\rho]$, where $\mathcal{L}[\rho]$ is the Liouvillian, which accounts for the dissipative processes of cavity loss, spin-lattice relaxation and spin dephasing.

$$\mathcal{L}[\rho] = \mathcal{L}_{\mathrm{cavity}}[\rho] + \mathcal{L}_{\mathrm{spin-lattice}}[\rho] + \mathcal{L}_{\mathrm{dephasing}}[\rho].$$

Spontaneous emission can been neglected since it is so small at microwave frequencies. Each component of the Liouvillian is given by:

$$\mathcal{L}_{\mathrm{cavity}}[\rho] = \frac{\kappa_{\mathrm{c}}}{2}\mathcal{D}[a]\rho \tag{3}$$

$$\mathcal{L}_{\mathrm{spin-lattice}}[\rho] = \frac{\gamma}{2}\sum_{j=1}^{N}\left(\mathcal{D}[\sigma_j^-]\rho + \mathcal{D}[\sigma_j^+]\rho\right) \tag{4}$$

$$\mathcal{L}_{\mathrm{dephasing}}[\rho] = \frac{\kappa_{\mathrm{s}}}{2}\sum_{j=1}^{N}\mathcal{D}[\sigma_j^z]\rho \tag{5}$$

where $\mathcal{D}[\mathcal{O}]\rho = 2\mathcal{O}\rho\mathcal{O}^\dagger - \mathcal{O}^\dagger\mathcal{O}\rho - \rho\mathcal{O}^\dagger\mathcal{O}$ is the Lindblad superoperator, $\kappa_{\mathrm{c}} = \omega_{\mathrm{c}}/Q$ is the cavity photon decay rate, γ is the spin-lattice relaxation rate and $\kappa_{\mathrm{s}} = 2/T_2$ is the spin dephasing rate. An exact expression for the rate of change of the expectation value for the cavity photon number $\langle n\rangle = \left\langle a^\dagger a\right\rangle$ can be derived from Eq. 1:

$$\frac{d}{dt}\langle a^\dagger a\rangle = -\kappa_{\mathrm{c}}\langle a^\dagger a\rangle + \kappa_{\mathrm{c}}\bar{n} + igN\left(\langle\sigma_1^+ a\rangle - \langle a^\dagger\sigma_1^-\rangle\right) \tag{6}$$

where $\bar{n} = 1/(e^{\hbar\omega_{\mathrm{c}}/kT} - 1)$ is the average thermal photon population in the cavity. The average photon number $\langle n\rangle = \langle a^\dagger a\rangle$ couples to the spins through the last term, the spin-photon coherence $\langle\sigma_1^+ a\rangle = \langle a^\dagger\sigma_1^-\rangle^*$. As one would expect the photon number decays with rate κ_{c}. The spin-photon coherence rate is

$$\frac{d}{dt}\langle\sigma_1^+ a\rangle = -\left(\frac{\kappa_{\mathrm{c}}}{2} + \frac{\gamma}{2} + \frac{\kappa_{\mathrm{s}}}{2} + i\Delta\right)\langle\sigma_1^+ a\rangle - ig_{\mathrm{s}}\left[\frac{\langle\sigma_1^z\rangle + 1}{2} + (N-1)\langle\sigma_1^+\sigma_2^-\rangle + \langle a^\dagger a\rangle\langle\sigma_1^z\rangle\right] \tag{7}$$

where third order cumulants and higher have been neglected and $\Delta = \omega_{\mathrm{c}} - \omega_{\mathrm{s}}$ is the frequency detuning parameter. Note that since the system is not being driven or pumped by coherent fields, there is no well-defined phase so that we can take $\langle a\rangle = \langle a^\dagger\rangle = \langle\sigma_1^\pm\rangle = 0$. The rate of change of the inversion $\langle\sigma_1^z\rangle$ is also exact:

$$\frac{d}{dt}\langle\sigma_1^z\rangle = -\gamma\langle\sigma_1^z\rangle - 2ig_{\mathrm{s}}\left(\langle\sigma_1^+ a\rangle - \langle a^\dagger\sigma_1^-\rangle\right) \tag{8}$$

and finally, the set of equations is closed by the spin-spin correlation:

$$\frac{d}{dt}\langle\sigma_1^+\sigma_2^-\rangle = -(\gamma+\kappa_\mathrm{s})\langle\sigma_1^+\sigma_2^-\rangle + ig_\mathrm{s}\langle\sigma_1^z\rangle\left(\langle\sigma_1^+a\rangle - \langle a^\dagger\sigma_1^-\rangle\right), \tag{9}$$

where again third-order terms have been neglected.

In terms of normalized collective spin operators:

$$\tilde{S}^\pm = \frac{1}{\sqrt{N}}\sum_i^N \sigma_i^\pm, \qquad \tilde{S}^z = \frac{1}{N}\sum_i^N \sigma_i^z = \frac{1}{N}S^z,$$

the closed set of coupled equations become:

$$\begin{aligned}
\frac{d}{dt}\langle a^\dagger a\rangle &= -\kappa_\mathrm{c}\langle a^\dagger a\rangle + \kappa_\mathrm{c}\bar{n} + ig_\mathrm{e}\left(\langle\tilde{S}^+a\rangle - \langle a^\dagger\tilde{S}^-\rangle\right)\\
\frac{d}{dt}\langle\tilde{S}^+a\rangle &= -\left(\frac{\kappa_\mathrm{c}}{2}+\frac{\gamma}{2}+\frac{\kappa_\mathrm{s}}{2}+i\Delta\right)\langle\tilde{S}^+a\rangle - ig_\mathrm{e}\left[\frac{\langle\tilde{S}^z\rangle+1}{2} + \left(1-\frac{1}{N}\right)\langle\tilde{S}^+\tilde{S}^-\rangle + \langle a^\dagger a\rangle\langle\tilde{S}^z\rangle\right]\\
\frac{d}{dt}\langle\tilde{S}^z\rangle &= -\gamma\langle\tilde{S}^z\rangle - 2ig_\mathrm{e}\frac{1}{N}\left(\langle\tilde{S}^+a\rangle - \langle a^\dagger\tilde{S}^-\rangle\right)\\
\frac{d}{dt}\langle\tilde{S}^+\tilde{S}^-\rangle &= -(\gamma+\kappa_\mathrm{s})\langle\tilde{S}^+\tilde{S}^-\rangle + ig_\mathrm{e}\langle\tilde{S}^z\rangle\left(\langle\tilde{S}^+a\rangle - \langle a^\dagger\tilde{S}^-\rangle\right)
\end{aligned}$$

where $g_\mathrm{e} = g_\mathrm{s}\sqrt{N}$ is the collective spin-photon coupling. Given initial conditions $\langle a^\dagger a\rangle = \bar{n} \sim 4.3\times10^3$, $\langle\tilde{S}^+a\rangle = 0$, $\langle\tilde{S}^z\rangle = 0.8$, $\langle\tilde{S}^+\tilde{S}^-\rangle = 0$ and suitable values for the single-spin photon coupling g_s, cavity decay rate κ_c, spin decoherence rate κ_s and number of spins N, the set of equations can be integrated in time, using for example the Runge-Kutta method, to reveal the dynamics of the expectation values.

Pentacene:*p*-terphenyl crystal growth

Commercially available pentacene powder (TCI Europe NV) was vacuum purified and *p*-terphenyl commercial powder (Alfa Aesar, 99%+, AL4833) was zone-refined. 0.053% mol/mol pentacene in *p*-terphenyl powder was prepared and sealed in a 3 mm inner diameter surface modified quartz ampoule with vacuum level of around 10^{-3} mbar. A sharp tip was made at one of end of the ampoule for self-seeding. The wall surfaces of the ampoule were coated with 1H,1H,2H,2H-perfluorodecyltrichlorosilane (FDTS) and cleaned thoroughly using solvents (acetone, isopropanol and distilled water) in an ultrasonic bath. A zone melting technique was used to grow the pentacene-doped *p*-terphenyl crystal. An in-house furnace's temperature was controlled with a Eurotherm 3216 temperature controller and TE10A power controller to conduct the zone melting process at a temperature of 200 °C. The melt zone temperature was set at 230 °C. The ampoule was lowered through the furnace at a rate of around 1 mm per hour using a gear motor. Thereafter, the furnace was cooled down at 1 °C per hour to room temperature and the ingot retrieved. Due to the manner of crystal growth (habit), the triclinic *c*-plane exists along the ampoule long-axis.

SUPPLEMENTARY REFERENCES

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