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 \( \sim 2.5 \) 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’ \( C = g_e^2/\kappa_s\kappa_c \) is a good figure of merit, yet by no means the criterion for strong-coupling, which is \( g_e \gg \kappa_c, \kappa_s \), where \( g_e \) is the ensemble spin-photon coupling, \( \kappa_s \) and \( \kappa_c \) 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 \( g_e = g_s \sqrt{N} = \gamma \sqrt{\mu_0 \omega_c N/2V_m} \), where \( \mu_0 \) is the permeability of free-space, \( \hbar \) is the reduced Planck constant, \( \omega_c \) 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, $\frac{1}{2}\mu_0 \int_V |H(r)|^2 dV$ to the maximum magnetic field energy density, $\frac{1}{2}\mu_0 |H(r)|^2$. Factoring out parameters that are independent of the cavity, like the number of spins $N$ and the spin decoherence rate $\kappa_s$, reduces the ‘cavity cooperativity’ to

$$C_{cav} \propto \frac{g_s^2}{\kappa_c} \propto \frac{\omega_c}{\kappa_c V_m} \propto \frac{Q}{V_m},$$

which is proportional to the Purcell factor [2] for a given frequency $\omega_c$:

$$F_m = \frac{2\pi c^3}{\omega_c^3} \cdot \frac{Q}{V_m}.$$
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\(_2\)O\(_3\)) 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 \( \varepsilon_r = 318 \) and that of sapphire is \( \varepsilon_r = 9.3 \). 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 \( 9 \times 10^{-5} \) and \( 2 \times 10^{-6} \) at 1.45 GHz respectively. The surface resistance of the copper shield was 10 m\( \Omega \). The fundamental TE\(_{011}\) 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 $H(r)$ within the cavity can be directly mapped onto to the coupling strength for an individual spin to a vacuum cavity photon, $g_{rms}(r) = \mu_0 \gamma H(r)_{vac}$, where $\gamma$ is the electron gyromagnetic ratio, $\mu_0$ is the permeability of free-space and the vacuum magnetic field in the cavity is given by $H(r)_{vac} = \sqrt{\hbar \omega_c/2 \mu_0 \int_V |H(r)|^2 dV \cdot |H(r)|}$. 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 $|r| < 1.5 \text{ mm}$, $|z| < 2 \text{ mm}$, the spin-photon coupling is $g_s/2\pi = 0.042 \pm 0.002 \text{ Hz}$.

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 $|r| < 1.5 \text{ mm}$, $|z| < 2 \text{ mm}$, the spin-photon coupling is $g_s/2\pi = 0.042 \pm 0.002 \text{ Hz}$.

Master equations: decoherence and thermal noise

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

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

where $H$ is the Tavis-Cummings Hamiltonian:

$$H = \hbar \omega_c a^\dagger a + \frac{1}{2} \hbar \omega_b \sum_j^{N} \sigma_j^z + \hbar g_s \sum_j^{N} (\sigma_j^+ a + a^\dagger \sigma_j^-) \quad \text{(2)}$$
and $\rho$ 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.

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

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

$$\mathcal{L}_{\text{cavity}}[\rho] = \kappa_c D[a] \rho$$

$$\mathcal{L}_{\text{spin–lattice}}[\rho] = \frac{\gamma}{2} \sum_{j=1}^{N} (D[\sigma_j^-] \rho + D[\sigma_j^+] \rho)$$

$$\mathcal{L}_{\text{dephasing}}[\rho] = \frac{\kappa_s}{2} \sum_{j=1}^{N} D[\sigma_j^z] \rho$$

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

$$\frac{d}{dt} \langle a^\dagger a \rangle = -\kappa_c \langle a^\dagger a \rangle + \kappa_c \bar{n} + igN \left( \langle \sigma_1^+ \rangle - \langle a^\dagger \sigma_1^- \rangle \right)$$

where $\bar{n} = 1/(e^{\hbar \omega_c/kT} - 1)$ 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 $\kappa_c$. The spin-photon coherence rate is

$$\frac{d}{dt} \langle \sigma_1^+ a \rangle = -\left( \frac{\kappa_c}{2} + \frac{\gamma}{2} + \frac{\kappa_s}{2} + i\Delta \right) \langle \sigma_1^+ a \rangle - ig_s \left[ \frac{\langle \sigma_1^+ \rangle + 1}{2} + (N - 1) \langle \sigma_1^+ \sigma_2^- \rangle + \langle a^\dagger a \rangle \langle \sigma_1^z \rangle \right]$$

where third order cumulants and higher have been neglected and $\Delta = \omega_c - \omega_s$ 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 $\langle a \rangle = \langle a^\dagger \rangle = \langle \sigma_1^+ \rangle = 0$. The rate of change of the inversion $\langle \sigma_1^z \rangle$ is also exact:

$$\frac{d}{dt} \langle \sigma_1^z \rangle = -\gamma \langle \sigma_1^z \rangle - 2ig_s \left( \langle \sigma_1^+ \rangle - \langle a^\dagger \sigma_1^- \rangle \right)$$
and finally, the set of equations is closed by the spin-spin correlation:

\[
\frac{d}{dt} \langle \sigma_1^+ \sigma_2^- \rangle = - (\gamma + \kappa_s) \langle \sigma_1^+ \sigma_2^- \rangle + ig_s (\sigma_1^+ a - a^\dagger \sigma_1^-),
\]

where again third-order terms have been neglected.

In terms of normalized collective spin operators:

\[
\tilde{S}^\pm = \frac{1}{\sqrt{N}} \sum_i \sigma_i^\pm, \quad \tilde{S}^z = \frac{1}{N} \sum_i \sigma_i^z = \frac{1}{N} S^z,
\]

the closed set of coupled equations become:

\[
\frac{d}{dt} \langle a^\dagger a \rangle = -\kappa_c \langle a^\dagger a \rangle + \kappa_c \bar{n} + ig_e \left( \langle \tilde{S}^+ a \rangle - \langle a^\dagger \tilde{S}^- \rangle \right)
\]

\[
\frac{d}{dt} \langle \tilde{S}^+ a \rangle = - \left( \frac{\kappa_c}{2} + \frac{\gamma}{2} + \frac{\kappa_s}{2} + i\Delta \right) \langle \tilde{S}^+ a \rangle - ig_e \left[ \frac{\langle \tilde{S}^z \rangle + 1}{2} + \left( 1 - \frac{1}{N} \right) \langle \tilde{S}^+ \tilde{S}^- \rangle + \langle a^\dagger a \rangle \langle \tilde{S}^z \rangle \right]
\]

\[
\frac{d}{dt} \langle \tilde{S}^z \rangle = - \gamma \langle \tilde{S}^z \rangle - 2ig_e \frac{1}{N} \left( \langle \tilde{S}^+ a \rangle - \langle a^\dagger \tilde{S}^- \rangle \right)
\]

\[
\frac{d}{dt} \langle \tilde{S}^+ \tilde{S}^- \rangle = - (\gamma + \kappa_s) \langle \tilde{S}^+ \tilde{S}^- \rangle + ig_e \langle \tilde{S}^z \rangle \left( \langle \tilde{S}^+ a \rangle - \langle a^\dagger \tilde{S}^- \rangle \right)
\]

where \( g_e = g_s \sqrt{N} \) is the collective spin-photon coupling. Given initial conditions \( \langle a^\dagger a \rangle = \bar{n} \sim 4.3 \times 10^3, \langle \tilde{S}^+ a \rangle = 0, \langle \tilde{S}^z \rangle = 0.8, \langle \tilde{S}^+ \tilde{S}^- \rangle = 0 \) and suitable values for the single-spin photon coupling \( g_s \), cavity decay rate \( \kappa_c \), spin decoherence rate \( \kappa_s \) 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 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


