The strong coupling regime is essential for efficient transfer of excitations between states in different quantum systems on timescales shorter than their lifetimes. The coupling of single spins to microwave photons is very weak but can be enhanced by increasing the local density of states by reducing the magnetic mode volume of the cavity. In practice, it is difficult to achieve both small cavity mode volume and low cavity decay rate, so superconducting metals are often employed at cryogenic temperatures. For an ensembles of $N$ spins, the spin–photon coupling can be enhanced by $\sqrt{N}$ through collective spin excitations known as Dicke states. For sufficiently large $N$ the collective spin–photon coupling can exceed both the spin decoherence and cavity decay rates, making the strong-coupling regime accessible. Here we demonstrate strong coupling and cavity quantum electrodynamics in a solid-state system at room-temperature. We generate an inverted spin-ensemble with strongly coupled Dicke states

$\frac{\omega_c}{\Delta} \approx 10^{-4}$ by photo-exciting pentacene molecules into spin-triplet states with spin dephasing time $T_2 \approx 3 \mu s$. When coupled to a 1.45 GHz TE01 mode supported by a high Purcell factor strontium titanate dielectric cavity ($V_m \sim 0.25 \text{ cm}^3$, $Q \sim 8,500$), we observe Rabi oscillations in the microwave emission from collective Dicke states and a 1.8 MHz normal-mode splitting of the resultant collective spin–photon polariton. We also observe a cavity protection effect at the onset of the strong-coupling regime which decreases the polariton decay rate as the collective coupling increases.
The TE₀₁ mode with a much higher concentration of 0.053% mol/mol than in cylinder of STO, but houses a pentacene-doped for a miniaturised room-temperature maser which uses a hollow not be considered further. The cavity is similar to the one reported with small magnetic mode volume, which at zero magnetic fi has a magnetic field vector. c Region illuminated by optical pulse. The magnetic field directly maps to the single spin–photon coupling gₛ, for a cylindrical region of diameter 3 mm and height 4 mm, where the pentacene:p-terphenyl crystal resides. d Cartoon rendering of the cavity QED system. A 0.053% mol/mol pentacene-doped p-terphenyl crystal is housed within a hollow cylinder of strontium titanate inside a cylindrical copper enclosure. The fundamental TE₀₁ mode of the cavity is tuned to ~1.45 GHz, the transition frequency of the X and Z triplet sub-levels. The pentacene molecules are photo-excited by pulses from an optical parametric oscillator. Microwave power is coupled out from the cavity by a small antenna loop and directly recorded by a digital storage oscilloscope without amplification.

### RESULTS

In order to satisfy this condition at room-temperature, we utilise a system comprising spin-triplets in pentacene molecules to generate a polarised (inverted) population of N spins and a cavity with small magnetic mode volume, Vₘ ≈ 10⁻³λ³, where λ is the free-space wavelength (see Fig. 1d). Following photo-excitation of pentacene in zero magnetic field, the non-degenerate X, Y, Z sub-levels of the TE₀₁ spin-triplet are rapidly populated in the ratios 0.76 : 0.16 : 0.08, respectively¹⁷ (see Fig. 1a). Since the fluorescence lifetime of photo-excited singlet states in pentacene is ~9 ns and the intersystem crossing singlet-triplet quantum yield is 0.625,¹⁸ the singlet-triplet transition lifetime is expected to be ~14 ns. The initial inversion is S ° = 0.8N, where N is the number of pentacene molecules excited into either the |e⟩ ≡ |X⟩ or |g⟩ ≡ |Z⟩ states, which at zero magnetic field have a frequency splitting of ω₀/T₂ ≈ 1.45 GHz. The |Y⟩ state does not play a significant role and shall not be considered further. The cavity is similar to the one reported for a miniaturised room-temperature maser which uses a hollow cylinder of STO, but houses a pentacene-doped p-terphenyl crystal with a much higher concentration of 0.053% mol/mol than in previous studies.¹⁹,²⁰ The TE₀₁ mode has a frequency tuned to the |e⟩ ↔ |g⟩ spin transition, ω₀ ≈ 2π × 1.45 GHz. This mode has a magnetic field dipole directed along the cylindrical axis (Fig. 1b) which, via the S' spin-operator, induces transitions between the |e⟩ ↔ |g⟩ states in suitably aligned pentacene molecules. STO has a high electric permittivity (εᵣ ≈ 320) that allows a sub-wavelength (λ₀/18 ~ 1 cm) cavity to be constructed with a mode volume Vₘ of 0.25 cm³. An optical parametric oscillator (OPO) generated λ ~ 592 nm pulses of 5.5 ns duration and energy up to 15 mJ at a repetition rate of 10 Hz. The 4 mm diameter (Gaussian profile) beam of the OPO was focussed onto the 3 mm diameter pentacene-doped p-terphenyl crystal by the high refractive index (n ~ 2.6) of the STO. Numerical modelling of the penetration of optical pulses into the pentacene-doped p-terphenyl allowed the number N of excited pentacene molecules to be estimated¹⁸ and revealed that the spin-triplet yield is a linear function of the incident optical pulse energy (see Supplementary Information). For an optical pulse energy of 15 mJ, the number of pentacene molecules N excited into the |e⟩ and |g⟩ states was estimated to be ~7 × 10¹⁴, with an initial inversion S ° = 6 × 10¹⁴. The microwave magnetic energy-density (Fig. 1b) can be mapped directly to the single spin–photon coupling in the central region of the cavity housing the pentacene molecules (Fig. 1c). Within the region illuminated by the optical pulse, the single spin–photon coupling is gₛ/T₂ ≈ 0.042 ± 0.002 Hz. An estimate of the ensemble spin–photon coupling strength is therefore gₛ ≈ gₛ/Vₘ ~ 2π × 1.1 MHz. The cavity mode decay rate (linewidth) was measured to be κ₀T₂ ~ 2π/T₂ ~ 0.018 MHz and the spin decoherence rate of the transition was taken from reported room-temperature free induction decay measurements of the spin dephasing time for samples of similar concentration, T₂ ~ 2.9 μs,¹⁹ yielding a rate of κ₀T₂ ~ 2π × 0.11 MHz. The spin-lattice relaxation rate and decay rates of the triplet sub-levels back to the singlet ground state are at least an order of magnitude slower than the spin dephasing rate so can be neglected.²² Thus, the system is expected to be within the strong coupling regime since the predicted ensemble spin–photon coupling is an order of
DISCUSSION

For a single excitation on resonance ($\omega_c = \omega_0$), the eigenstates are a coherent superposition of two basis states: the spin mode and the cavity mode. If $|0\rangle_c$ and $|1\rangle_c = a^\dagger |0\rangle_c$ are the possible states of the cavity mode and $|0\rangle_s$ and $|1\rangle_s = a^\dagger |0\rangle_s$ are the possible states of the spin mode, then the two eigenstates are $|+\rangle = \frac{1}{\sqrt{2}} (|1\rangle_c |0\rangle_s + |0\rangle_c |1\rangle_s)$ and $|-\rangle = \frac{1}{\sqrt{2}} (|1\rangle_c |0\rangle_s - |0\rangle_c |1\rangle_s)$, separated in energy by $\hbar \Omega = 2g_n$. In this system, there are many more excitations so to describe the dynamical behaviour of the Dicke system we derived Lindblad master equations for the reduced spin–photon density matrix within the Born–Markov approximation. Here we used the Tavis–Cummings Hamiltonian and a Liouvillian that accounted for decoherence due to cavity decay, spin dephasing and spin-lattice relaxation. A system of coupled differential equations was derived for the expectation values of relevant variables using a cumulant expansion truncated to third-order (see Supplementary Information). The dynamical behaviour of the expectation values of the cavity photon population, spin–photon coherence, spin–spin correlation and inversion are shown in Fig. 3, where the photon population $n = \langle a^\dagger a \rangle$ is in excellent agreement with that inferred from the measured microwave power. The delay between photo-excitation and the emergence of the first microwave burst is due to a prolonged period of stimulated emission since the number of excitations in the initial spin inversion ($10^{15}$) greatly exceeds the number of thermal photons in the cavity mode ($10^3$). This period of stimulated emission results in a microwave photon burst where the cavity mode photon population has similar magnitude to the number of spins $N$. It is also accompanied by a build-up of the spin–spin correlation $\langle S^z S^z \rangle /N$. The spins are not correlated initially but through stimulated emission of photons into the cavity mode they become increasingly correlated, leading to the establishment of a macroscopic collective spin–photon polariton. The maximum expectation value of the modelled spin–spin correlation, $\langle S^z S^z \rangle /N \approx 0.15$ is close to the theoretical maximum of 0.25.

Fig. 2 Measurement of Rabi oscillations from photo-excited pentacene-p-terphenyl spin-ensemble coupled to the STO cavity. a Single-shot measurement of microwave output following optical pulse. The initial burst builds up from thermal photons and follows classical laws since the spin–spin correlation and spin–photon coherence has yet to build up. This was measured by directing the output microwave signal into an oscilloscope. b Instantaneous power of the output following optical pulse. The peak microwave output power is $-6.8 \text{ dBm}$. Subsequent oscillations in the microwave power, with period $0.55 \mu s$ and decay rate $\Gamma$, are due to the collective exchange of energy between the correlated ensemble Dicke state and the cavity mode. The blue line shows the expected decay of an empty cavity ($\propto e^{-\chi}$). c Fourier analysis of the signal for a cavity frequency of $\omega_c = 2\pi \times 1.4495 \text{ GHz}$ and 15 mJ optical pulse energy reveals that ensemble spin-coupling has split the normal modes, yielding a Rabi frequency of $\Omega \sim 2\pi \times 1.8 \text{ MHz}$. d Increasing the laser pulse energy excites more pentacene molecules into spin-triplets and therefore increases the ensemble spin (and hence normal-mode Rabi splitting) with a $\sqrt{N}$ dependence. This graph confirms that the square of the splitting is linearly dependent on the optical pump pulse energy and hence $N$.
The decay rate

tion value of the cavity photon number

tically towards half the cavity decay rate,

spin

ensemble spin
dephasing rate is suppressed. This so-called

subsequently oscillates through the Rabi cycles, coming to rest in a

cavity photon polariton decay rate

absorption of photons to speci

ment within the symmetric Dicke states. The entanglement

correspond
to exchange of excitations from the collective spins to the cavity

The discrepancy is mostly due to the imperfect initialisation of the

spin population polarisation. The collective spin–spin correlation

(\(\langle \mathbf{S}^+ \mathbf{S}^- \rangle\)) also reveals the degree of transient multipartite entangle

ment within the symmetric Dicke states. The entanglement resulting from the ambiguity in being able to assign emission or

absorption of photons to specific spins. For the

mode and positive values from the cavity mode to the collective

The authors declare that the main data supporting the

reporting method\(^{19,20}\) but with higher concentration of pentacene (see

Supplementary Information for details). To conclude, this system, which was recently used to
demonstrate a solid-state room-temperature maser\(^{19,20,23}\), also
shows promise as a platform for exploring cavity quantum

electrodynamics, spin memories for quantum information proces

sensing and communications.\(^{27}\)

METHODS

Experimental setup

The cavity was constructed from a hollow cylindrical single-crystal of STO

containing a 0.053% pentacene-doped \(-\)-terphenyl crystal (diameter 3 mm, height 8 mm). The STO cylinder was placed upon a cylindrical sapphire disc

and housed within a cylindrical copper enclosure. The cavity was directly
coupled to a digital storage oscilloscope with 50 \(\Omega\) impedance (Keysight

MSOX6004A, 20 GSa/s sampling-rate, 6 GHz bandwidth) using a small loop

antenna with coupling coefficient, \(k\) = 0.2. An additional weakly coupled

(\(-35 \text{ dB}\) antenna, directional coupler (\(-20 \text{ dB}\) and amplifier (40 dB)
allowed transmission measurements of the cavity to made using a vector

network analyser (Agilent 8520E), revealing the resonant frequency and

loaded quality-factor (\(Q\)) of the \(\text{TE}_{010}\) mode to be \(\omega_c \approx 2\pi \times 1.45 \text{ GHz and}

8,500 respectively. A Nd:YAG pumped OPO (Continuum Surelite Plus SL L:

20) generated 592 nm wavelength optical pulses of 5.5 ns duration and energy up to 15 mJ at a repetition rate of 10 Hz. The optical pulse

envelopes were measured using a beam splitter and an optical energy metre

(Gentec-EO Maestro). The expectation value of the photon number as a function of time was extracted from the measured microwave power \(P(t)

using the expression \(\pi(t) = \langle a^\dagger a \rangle = P(t)/(1 + k)/h\omega_c k\), where \(k\) is the

coupling coefficient (\(k = 0.2\)), \(h\) is the reduced Planck constant and \(\omega_c\) and

\(k\), the cavity frequency and decay rate respectively.

Crystal growth

The pentacene-\(-\)-terphenyl crystal was grown as per the previously reported method\(^{9,35}\) but with higher concentration of pentacene (see

Supplementary Information for details).

Data availability

The authors declare that the main data supporting the finding of this study
are available within the article and its Supplementary Information files.
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AUTHOR CONTRIBUTIONS
Experiments were performed by J.D.B., E.S., J.S. and C.W.M.K. Data was processed by J.D.B. and C.W.M.K. Theory was developed by J.D.B. who also performed simulations of quantum master equations, optical pulse penetration and cavity design. The paper was written by J.D.B., assisted by C.W.M.K. and with additional editing by E.S. and N.M. A. The study was conceived by J.D.B., E.S., N.M.A. and C.W.M.K.

ADDITIONAL INFORMATION
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