An organic quantum battery

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Quantum batteries harness the unique properties of quantum mechanics to enhance energy storage compared to conventional batteries. In particular, they are predicted to undergo superextensive charging, where batteries with larger capacity actually take less time to charge\textsuperscript{1-4}. Up until now however, they have not been experimentally demonstrated, due to the challenges in quantum coherent control. Here we implement an array of two-level systems coupled to a photonic mode to realise a Dicke quantum battery. Our quantum battery is constructed with a microcavity formed by two dielectric mirrors enclosing a thin film of a fluorescent molecular dye in a polymer matrix. We use ultrafast optical spectroscopy to time resolve the charging dynamics of the quantum battery at femtosecond resolution. We
experimentally demonstrate superextensive increases in both charging power and storage capacity, in agreement with our theoretical modelling. We find that decoherence plays an important role in stabilising energy storage, analogous to the role that dissipation plays in photosynthesis. This experimental proof-of-concept is a major milestone towards the practical application of quantum batteries in quantum and conventional devices. Our work opens new opportunities for harnessing collective effects in light-matter coupling for nanoscale energy capture, storage, and transport technologies, including the enhancement of solar cell efficiencies.

Conventional batteries operate on the basis of classical electrochemical principles developed in the eighteenth century. Quantum batteries (QB) represent a new class of energy storage devices that instead operate on distinctly quantum mechanical principles. In particular, they are driven either by quantum entanglement, that reduces the number of traversed states in the Hilbert space compared to (classical) separable states alone, or by cooperative behaviour that increases the effective quantum coupling between battery and source.

System properties can typically be categorised as intensive (i.e. they are independent of the system size, such as density) or extensive (i.e. they grow in proportion to system size, such as mass). QBs exhibit a counter-intuitive property where the charging time is inversely related to the battery capacity. This leads to the intriguing idea that the charging power of QBs is superextensive; that is, it increases faster than the size of the battery. Typically consisting of a collection of $N$ identical quantum subsystems to which an external energy source is applied, QBs have been predicted to exhibit superextensive charging rate density (charging rate per subsystem) that scales as $N$ or $\sqrt{N}$ in the thermodynamic limit; therefore, the total charging rate grows faster than the system size. If experimentally verified, this would have important implications for energy storage and capture technologies. However, there are challenges in engineering the precise
environment in which such behaviour can occur, and in monitoring the ultrashort charging time scales.

Here we experimentally realise a Dicke QB\textsuperscript{19} (DQB) using an organic semiconductor as an ensemble of two-level systems (TLSs) coupled to a confined optical mode in a microcavity. This provides a practical version of the DQB which uses the optical cavity mode to induce collective coupling between light and the molecules. In this device, constructive interference of different absorption processes leads to enhanced transition rates, analogous to superradiant emission\textsuperscript{20} and superabsorption\textsuperscript{21}. We demonstrate how dissipation plays a crucial role in the performance of our DQB. In a closed system, the coherent effects that lead to fast charging can also lead to subsequent fast discharging. In our open noisy system, dephasing enables a \textit{ratchet} effect, where excited states are capable of absorbing but not losing energy\textsuperscript{22}, thereby retaining the stored energy until it can be used.

\textbf{Quantum battery structure}

The fabricated DQBs consist of a thin layer of a low-mass molecular semiconductor dispersed into a polymer matrix that is deposited by spin-coating and positioned between two dielectric mirrors, forming a microcavity as illustrated schematically in Fig. 1a (see Methods section for fabrication details). Organic semiconductors are particularly promising for many applications as the high oscillator strength and binding energy of molecular excitons means that light can be absorbed efficiently and excitons can exist at room temperature\textsuperscript{23}. The organic semiconductor used in this study was the dye Lumogen-F Orange (LFO), whose chemical structure is shown in Fig. 1b. The normalised absorption and photoluminescence spectra for LFO dispersed at 1\% concentration by mass in a polystyrene (PS) matrix are shown in Fig. 1b. By diluting the LFO, we reduce intermolecular interactions that lead to emission quenching, producing a high photoluminescence quantum yield of around 60\% at low concentration (see Extended
Data Fig. 1). The absorption peak at 526 nm and the emission peak at 534 nm correspond to the 0-0 transition, i.e. an electronic transition to and from the lowest vibrational state. Operating around the 0-0 transition, the LFO molecules can reasonably be considered as a TLS. We prepared samples with 0.5%, 1%, 5%, and 10% concentrations, as these are representative of the optimal operating regimes - further increases in concentration lead to quenching, and signals from lower concentrations are indiscernible from noise. The absorption and photoluminescence spectra for the 0.5%, 5% and 10% concentrations are given in Extended Data Fig. 2.

**Fig. 1 Schematics of the LFO microcavity and experimental setup.** (a) Microcavity consisting of Lumogen-F Orange (LFO) dispersed in a polystyrene (PS) matrix between distributed Bragg...
reflectors (DBRs). (b) Normalised absorption (red) and photoluminescence (blue) spectra for 1% concentration LFO film, with the molecular structure shown in the inset. We operate near peak absorption/photoluminescence. (c) Angle-dependent reflectivity of the 1% cavity, with a fit for the cavity mode shown by the blue dashed line. (d) A laser pump pulse excites the LFO molecules. The energetics of the molecules are then measured with probe pulses delayed by time $t$, from which we can ascertain the peak energy density ($E_{\text{max}}$), rise time ($\tau$), and peak charging power ($P_{\text{max}}$). (e) The experimental setup for ultrafast transient reflectivity measurements. The output of a non-collinear optical parametric amplifier (NOPA) is split to generate pump (dark green) and probe (light green) pulses. A mechanical chopper is used to modulate the pump pulse to produce alternating pump-probe and probe-only pulses.

The optical microcavities fabricated support cavity modes whose energy is determined by the optical-thickness of the LFO layer and the penetration of the optical field into the cavity mirrors\textsuperscript{24}. The confined photon field drives coherent interactions with the molecules, which underpin the collective effects of the DQB. The LFO concentration dictates the operating coupling regime, with the 0.5% and 1% LFO cavities operating in the weak coupling regime, the 5% in the intermediate coupling regime, and the 10% in the strong coupling regime (see Extended Data Fig. 2 and discussion in Methods).

**Experimental setup**

The charging and energy storage dynamics of the DQB were measured using ultrafast transient-absorption (TA) spectroscopy\textsuperscript{25}, allowing femtosecond charging times to be measured. In this technique, we excite the DQB with a pump pulse, and then measure the evolution of stored energy (corresponding to the number of excited molecules) with a second probe pulse, delayed by time $t$ (Fig. 1d). The probe pulse is transmitted through the top distributed Bragg reflector (DBR) of the cavity, and the reflection from the bottom DBR is measured. The differential reflectivity induced by the pump-pulse is given by
\[
\frac{\Delta R}{R}(t) = \frac{R_{ON}(t) - R_{OFF}}{R_{OFF}},
\]

(3)

where \(R_{ON}\) (\(R_{OFF}\)) is the probe reflectivity with (without) the pump excitation. Note that control films are measured under differential transmittivity \(\Delta T / T\).

In our experimental setup (shown schematically in Fig. 1e), TA measurements were performed in a degenerate, almost collinear configuration. Pump and probe pulses were generated by a broadband non-collinear optical parametric amplifier (NOPA)\(^{26}\) and spanned the wavelength range 500 to 620 nm with a nearly transform-limited sub-20-fs duration (further details in Methods). An optical delay line was used to control the probe delay time, and a mechanical chopper was used to modulate the pump pulse, providing alternating probe-only and pump-probe pulses, allowing us to measure pump-induced absorption changes. Measurements at different molecular concentrations were performed, adjusting the pump fluence in order to maintain an approximately constant photon density (i.e. pump photons per LFO molecule) \(r = kN_\gamma / N\), where \(N\) is the total number of molecules in the excitation volume, \(N_\gamma\) is the total number of pump laser photons, and \(k\) is the fraction of them that actually reach the active layer of DQB. We estimate from the reflectivity data that only 6% to 8% of the initial pump excitation enters the cavity.

**Results**

We first show that ultrafast TA spectroscopy can monitor the population of excited molecules, even in a cavity, by comparing the control film and the DQB spectra as shown in Fig. 2a. The control film \(\Delta T / T\) spectra are shown for various probe delays (0.4 to 10 ps), and the \(\Delta R / R\) spectra of the DQBs are shown at a delay of 1.25 ps. The control film spectra show two positive bands around 530 and 577 nm, which both reflect excited state populations. By comparison with the spectra in Fig.1b, we attribute the 530
nm band to ground state bleaching (GSB) – i.e. suppression of absorption due to molecules already being in their excited state. The 577 nm band instead corresponds to stimulated emission (SE) by excited molecules. For each of the DQB spectra, we have a single prominent peak, which corresponds to the transient signal filtered by the cavity mode. This implies that the time-dependent transient reflectivity signal is proportional to the change in the number of excited molecules created by the pump\textsuperscript{27}, i.e. $\frac{\Delta R}{R}(t) \propto N_1(t)$.

By normalising the peak value of $\Delta R/R$ to $\hbar \omega N_1^{\text{max}}/N$, we can directly relate $\frac{\Delta R}{R}(t)$ to the temporal behaviour of the stored energy density of the DQB: $E(t) = \hbar \omega N_1(t)/N$, where $\omega$ is the molecular electronic transition frequency (taken to be equal to the cavity frequency). $N_1^{\text{max}}$ is calculated through theoretical modelling. We also note that two of the DQB spectra show a negative $\Delta R/R$ band, which results from the change in the refractive index induced by the pump pulse\textsuperscript{28}.

Figure 2b shows the experimental values for the time-dependent stored energy density in the DQBs. In all DQB\'s studied, the energy density undergoes a rapid rise followed by slow decay. The timescale of the rapid rise varies with concentration. We adjust the laser power to fix photon density $r$ across comparable DQB samples, and compare behaviour with different LFO concentrations. We found that to achieve a sufficiently high signal-to-noise ratio, it was not possible to compare all DQB\'s at the same $r$ value; instead, a constant $r$ value was maintained for matched DQB\'s. Specifically, measurements were made on DQB\'s with LFO concentrations of 10\%, 5\% and 1\% with approximately constant $r \approx 0.14$ (respectively labelled A1, A2, and A3), and 1\% and 0.5\% with $r \approx 2.4$ (labelled B1 and B2).
Fig. 2 Experimental demonstration of the superextensive charging of the Dicke quantum battery. (a) Differential-transmittivity ($\Delta T/T$) spectra for the control film at various probe delay times, and the differential-reflectivity ($\Delta R/R$) spectra for the DQBs at 1.25 ps probe delay. (b) Temporally resolved energy density of the DQBs. A1, A2 and A3 label results for DQBs containing LFO at concentrations of 10%, 5% and 1%, as the ratio of pump photons to
molecules is kept approximately constant at \( r \approx 0.14 \). B1 and B2 label measurements for LFO at concentrations of 1\% and 0.5\%, with \( r \approx 2.4 \). The use of two different \( r \) values was necessary to achieve a sufficiently high-signal-to-noise ratio. Points mark the experimental data, while continuous solid lines are the results of the theoretical model.

Overlaying the experimental data are the corresponding theoretical predictions (see Theoretical Model section), convolved with a Gaussian response function of \( \sim 120 \) fs full-width-at-half-maximum, to account for both the instrument response time (\( \sim 20 \) fs) and the cavity photon lifetime (which was extracted from the linewidth of the cavity mode). Although the signal-to-noise ratio is not sufficiently high to discern the predicted oscillatory behaviour in the A1 and A2 data, there is otherwise good agreement between the experimental data and the corresponding theoretical model.

To obtain the energetic dynamics of the DQBs, we take away the response function from the theoretical fit, as shown in Extended Data Fig. 3. Extended Data Table 1 summarises the rise time or the time to reach half maximum energy (\( \tau \)), the battery capacity or peak stored energy density (\( E_{\text{max}} \)), and the battery charging rate or peak charging power density \( [P_{\text{max}} = \max (dE / dt)] \) of the data presented in Figs. 2b. The data shows that \( \tau \) decreases with \( N \), whilst \( E_{\text{max}} \) and \( P_{\text{max}} \) increase with \( N \). Recalling that \( E_{\text{max}} \) and \( P_{\text{max}} \) are the stored energy and charging power \textit{per molecule}, this indicates superextensive behaviour. The scaling with \( N \) is not the same across all experiments. We define an effective power-law scaling of observables \( q_i \in \{ \tau, E_{\text{max}}, P_{\text{max}} \} \) in experiment \( i \) by the relation \( q_i / q_j = (N_i/N_j)^{f_q} \). As all our observables are intensive (i.e. densities), \( f_q > 0 \) indicates superextensive behaviour, \( f_q = 0 \) indicates extensive, and \( f_q < 0 \)
subextensive behaviours. Table 1 gives the observed values of $f_q$. The different values of $f_q$ are explained in the Theoretical Model section.

Our results demonstrate that as the size of the DQB increases, its charging time remarkably decreases whilst also increasing its stored energy density. This means that it takes less time to charge a single $N$-molecule DQB, than it would to charge $N$ single-molecule DQBs, even if the latter were charged simultaneously. Furthermore, one DQB with $N$ molecules would store more energy than $N$ DQBs, where each DQB contained a single molecule. These superextensive DQB properties are the key experimental findings of our work, and are supported by the theoretical modelling presented in the next section.

| Exp. | $f_\tau$ | $f_{\text{E}_{\text{max}}}$ | $f_{\text{P}_{\text{max}}}$ |
|------|----------|-----------------|-----------------|
| $A1/A2$ | $-$0.46 | 0.07 | 0.69 |
| $A2/A3$ | $-$0.40 | 0.62 | 1.08 |
| $B1/B2$ | $-$0.39 | 1.73 | 2.14 |

Table 1: Observed subextensive and superextensive scaling behaviours in rise-time, stored energy, and charging power. Power-law exponent $f_q$ (see text) for observable $q \in \{\tau, E_{\text{max}}, P_{\text{max}}\}$, where $f_q > 0$, $f_q = 0$, $f_q < 0$ indicates superextensivity, extensivity, and subextensivity, respectively. Table values indicate that charging time $\tau$ is subextensive, whilst stored energy $E_{\text{max}}$ and charging power $P_{\text{max}}$ are superextensive. The first column indicates the corresponding experiments.

**Theoretical Model**

The experimental dynamics of the DQBs can be reproduced by modelling, with the Lindblad master equation (LME), the $N$ TLSs in an optical cavity with light-matter coupling strength $g$, a driving laser with a Gaussian pulse envelope and peak amplitude
\( \eta_0 \), and three decay channels corresponding to the cavity decay (\( \kappa \)), TLS dephasing (\( \gamma^z \)), and TLS relaxation (\( \gamma^- \)). To solve this many-body LME, we make use of the cumulant expansion\textsuperscript{29-31}, with model parameters given by a chi-squared minimisation of the experimental data. Experimental uncertainties are estimated from the point-to-point variance of the data. Further details can be found in the Methods and Supplementary Information.

From our cumulant expansion simulations, we show how \( \tau, E_{\text{max}}, \) and \( P_{\text{max}} \) vary as a function of \( N \) in Fig. 3a and b. The interplay amongst the decay channels, driving laser, and cavity couplings give rise to a rich set of behaviour. We identify three regimes: decay-dominated at small \( N \), and coupling-dominated at large \( N \), along with a crossover regime between them. Figures 3c and d show the typical time dependence of the DQB in decay-dominated and coupling-dominated regimes, indicating how the model parameters affect the dynamics. In particular, the presence of the decay channels gives rise to ratchet states which are capable of absorbing but not emitting light\textsuperscript{22}, thereby allowing the energy to be stably stored in the battery. See Methods and Supplementary Information for further discussion on the operating regimes. Figure 3 is augmented with an animation of how the energetic dynamics of the DQB changes with \( N \) (see Supplementary Video).

Figures 3a and b provide an explanation for the scaling factors in Table 1. Specifically, A1 and A2 operate in the coupling-dominated regime, where \( \tau \) scales slightly less than \( N^{-1/2} \), \( E_{\text{max}} \) scales slightly more than \( N^0 \), and \( P_{\text{max}} \) scales slightly more than \( N^{1/2} \). For the region between A2 and A3, the average scaling of \( \tau \) falls between \( N^0 \) and \( N^{-1/2} \), \( E_{\text{max}} \) between \( N^2 \) and \( N^0 \), and \( P_{\text{max}} \) between \( N^2 \) and \( N^{1/2} \). As A2 is further in the coupling-dominated regime than A3 is in the decay-dominated regime, the average scaling values between A2 and A3 are skewed towards the coupling-dominated scalings.
B1 and B2 operate in the cross-over regime, with average scaling factors that are between the decay-dominated and coupling-dominated scalings, as reflected in Table 1.

**Fig. 3: Operating regimes of the quantum batteries.** (a) and (b) show the theoretical model (solid line) for \( r = 1.4 \) and 2.4, respectively. We show three operating regimes: decay-dominated (purple), coupling-dominated (green), and a decay-coupling-crossover regime. The decay-dominated regime is bounded by \( N_\kappa < \kappa^2/g^2r' \), and the coupling-dominated regime is bounded by \( N_{\gamma^z} > \gamma^{z2}/g^2r' \), where \( r' = \max(1, r) \). The coloured dots indicate where the experiments sit on these curves. The uncertainty in \( N \) is 10%, which is smaller than the dot size. (c) qualitatively depicts the effects of the model parameters in shaping the dynamics in the decay-
dominated regime. (d) qualitatively depicts the effects of the additional model parameters in shaping the dynamics in the coupling-dominated regimes.

**Summary**

We have demonstrated the operation of an open-system DQB driven by an external coherent light source and shown regimes of superextensive behaviour using ultrafast optical spectroscopy. We have provided direct experimental evidence of superextensive energy storage capacity and charging in the decay- and coupling-dominated regimes. Our realisation of a prototype QB highlights the fact that purely closed unitary dynamics is insufficient for realising a practical QB. The retention of energy requires finely-tuned decoherence processes, allowing the battery to charge quickly and yet discharge much more slowly. Our observation of such ratchet-type behaviour shows that realistic noisy environments are crucial for the implementation and application of useful QBs.

A prime example of how QBs could be applied to enhance existing technologies is in the field of solar energy conversion. The efficient solar energy harvesting that happens in natural photosynthesis derives from the intricate interplay of coherent and dissipative dynamics that we also exploit in our QB design, and we may learn further lessons from nature for improving QBs. Further, QBs could be made to charge more efficiently by surrounding them with antenna molecules that capture light through superabsorption\textsuperscript{21,32,33}. Since the working principle of DQBs is closely related to superabsorbing behaviour, it may be possible to generate even faster charging by using environmental engineering and control approaches. These could keep the QB operating in the range of higher-lying energy states that are associated with maximum absorption enhancement, i.e. near the mid-point of the Dicke ladder\textsuperscript{22}. Although our QB was charged...
by a coherent laser source, it opens a pathway for charging with incoherent sunlight, offering an exciting new approach to the design of solar-cell technology.

**Methods**

**Quantum battery fabrication**

The microcavities constructed consist of a thin layer of LFO (Kremer Pigmente) dispersed in a PS (Sigma-Aldrich, average molecular weight ~ 192,000) matrix. The bottom DBR consisted of 10 pairs of SiO$_2$/Nb$_2$O$_5$ and were fabricated using a mixture of thermal evaporation and ion-assisted electron beam deposition by HeliaPhotonics Ltd. Solutions of LFO dissolved in 25 mg/mL PS in dichloromethane were prepared at 0.5%, 1%, 5%, and 10% concentration by mass. Each LFO solution was then spin-coated on top of the bottom DBR to produce a thin film with an approximate thickness of 185 nm. An 8-pair DBR was then deposited on top of the LFO layer using electron beam deposition. With this pair of mirrors, the reflectivity was >99% in the spectral region of interest$^{34}$.

The diluted molecules are expected to be isolated at low concentration 0.1 – 1%, but at higher dye concentrations, the 0-0 emission transition red-shifts by a few nm and the second peak increases in intensity due to aggregation of the dye molecules. This is evident in Extended Data Fig. 2a and b, with additional broader features observed at longer wavelengths, which we assign to intermolecular states such as excimers.

The 0.5% and 1% cavities lie in the weak-coupling regime, i.e. no polaritonic splitting could be seen in the cavity reflectivity spectrum, as shown in Extended Data Fig. 2. For the 5% cavity, we see a weak anti-crossing feature in the reflectivity spectrum (a small kink near the crossing), indicating operation in the intermediate coupling regime. The 10% cavity operated in the strong-coupling regime, showing a Rabi splitting of
around 100 meV around the 0-0 transition (along with intermediate-coupling between the cavity mode and the 0-1 transition).

Extended Data Fig. 4 shows a transfer matrix simulation of the electric field distribution of the 1% cavity (the cavities exhibit similar distributions).

**Pump-probe spectroscopy**

Probe and pump pulses were generated by a broadband non-collinear optical parametric amplifier (NOPA). The NOPA was pumped by a fraction (450 μJ) of the laser beam generated by a regeneratively amplified Ti:Sapphire laser (Coherent Libra) producing 100 fs pulses at 800 nm at a repetition rate of 1 kHz. A pair of chirped mirrors were placed at the output of the NOPA to compensate for temporal dispersion, and by using 7 ‘bounces’ we were able to generate pulses with a temporal width below 20 fs. The laser beam was then split by a beam-splitter, with the probe being delayed via a translation stage and the pump being modulated mechanically using a chopper at 500 Hz.

**Number of molecules in film**

To determine the number of LFO molecules in the DQBs, we first determined the absorption cross-section of a single LFO molecule, $\sigma_{LFO}$. The transmission spectrum of a 0.1% solution of LFO in 25 mg/mL PS/dichloromethane in a 1 mm thick cuvette was measured using a Horiba Fluoromax 4 fluorometer with a xenon lamp. The absorption coefficient ($\alpha = n\sigma_{LFO}$) of the 0-0 transition was then calculated using the relation $T / T_0 = e^{-\alpha d}$, where $T / T_0$ is the fractional transmission of the xenon lamp at the 0-0 transition, $d$ is the cuvette thickness, $n$ is the number density of absorbing molecules in solution per unit volume, and $\sigma_{LFO}$ is the absorption cross-section of a single LFO
molecule\textsuperscript{35}. Using the known value of \( n \) for this solution, \( \sigma_{\text{LFO}} \) was calculated as \( 3.3 \times 10^{-16} \text{ cm}^2 \).

The transmission of the 10\% LFO concentration in film was then measured to obtain \( \alpha \) and hence \( n \) (number density of molecules in the cavity active layer), using the measured value of \( \sigma_{\text{LFO}} \), with \( d \) (film thickness) measured using a Bruker DektakXT profilometer. This value was then multiplied by the area of the laser beam and \( d \) to obtain \( N \). Here we assume a uniform distribution in the active layer. \( N \) for other concentrations were scaled accordingly.

**Lindblad master equation**

The open driven system of the experiment is modelled with the Lindblad master equation,

\[
\dot{\rho}(t) = -\frac{i}{\hbar}[H(t), \rho(t)] + \sum_{j=1}^{N} (\gamma^{+} \mathcal{L}[\sigma_{j}^{z}] + \gamma^{-} \mathcal{L}[\sigma_{j}^{-}]) + \kappa \mathcal{L}[a], \tag{2}
\]

where \( \rho(t) \) is the density matrix and \( \mathcal{L}[O] \equiv O \rho O^\dagger - \frac{1}{2}O^\dagger O \rho - \frac{1}{2} \rho O^\dagger O \) is the Lindbladian superoperator. \( a^\dagger \) and \( a \) are the cavity photon creation and annihilation operators, and \( \sigma_{j}^{x,y,z} \) are the Pauli spin matrices for each molecule, with the raising and lowering spin operators defined as \( \sigma_{j}^{\pm} = \sigma_{j}^{x} \pm i \sigma_{j}^{y} \). There are three decay channels corresponding to the cavity decay (\( \kappa \)), dephasing (\( \gamma^{z} \)), and relaxation rate (\( \gamma^{-} \)) of the individual TLSs. The Hamiltonian for the LFO molecules in cavity is modelled as a collection of non-interacting TLSs with characteristic frequency \( \omega \) equal to that of the cavity mode, and resonantly coupled to the cavity with strength \( g \). The molecules are driven by a laser described by a Gaussian pulse envelope \( \eta(t) = \frac{\eta_{0}}{\sigma \sqrt{2\pi}} e^{-\frac{1}{2} \left(\frac{t-t_{0}}{\sigma}\right)^{2}} \), and a carrier frequency \( \omega_{c} \). We work in the frame of the laser carrier frequency, and so write
\[
H(t) = \hbar \Delta a^+a + \sum_{j=1}^{N} \left[ \frac{\hbar \Delta}{2} \sigma_j^x + g (a^+ \sigma_j^- + a \sigma_j^+) \right] + i \hbar \eta(t)(a^+ - a),
\]

where \( \Delta = \omega - \omega_L \) is the detuning of the cavity frequency from the laser driving frequency. The LFO molecules are initially in the ground state, and the laser is on-resonance \( (\Delta = 0) \).

**Cumulant expansion**

The energy density of the cavity containing identical molecules with transition energy \( \omega \) is \( E(t) = \frac{\hbar \omega}{2} \left[ \langle \sigma^x(t) \rangle + 1 \right] \). In general, the equation of motion \( \frac{\partial}{\partial t} \langle \sigma^x \rangle = Tr[\sigma^x \dot{\rho}] \) depends on both the first order moments \( \langle \sigma^x \sigma^\pm \rangle \) and \( \langle a \rangle \) as well as higher order moments, leading to a hierarchy of coupled equations. Within mean field theory, the second order moments are factorised as \( \langle AB \rangle = \langle A \rangle \langle B \rangle \) which closes the set of equations at first order. This approximation is valid at large \( N \), as corrections scale as \( 1/N \). To capture the leading order effects of finite-sizes we make a second-order cumulant expansion\textsuperscript{29-31}, i.e. we keep second-order cumulants \( \langle \langle AB \rangle \rangle = \langle AB \rangle - \langle A \rangle \langle B \rangle \) and assume that the third-order cumulants vanish, which allows us to rewrite third-order moments into products of first and second-order moments\textsuperscript{36}. In our experiments, the number of molecules in the cavity is large \((>10^{10})\) and we find higher order correlations are negligible. We give the equations of motion up to second order in the Supplementary Information.

**Operating regimes**

The decay-dominated (purple region in Fig. 3a and b) regime occurs when the collective light-matter coupling is weaker than the decay channels, \( g \sqrt{N r'} < \{ \kappa, \gamma^z, \gamma^- \} \), where \( r' = \max(1, r) \). In this regime, the time scale of cavity dynamics is slow relative to the decay rate. Fig. 3c shows a typical time dependence of the DQB in this regime,
indicating how the model parameters affect the dynamics. In this regime, the increase in the effective coupling relative to the decay strength sees an $N^2$ superextensive scaling of the energy and power density, while rise time remains constant. Experiment A3 operates near the boundary of this regime (Fig. 3a).

In the coupling-dominated (green region in Fig. 3a and b) regime, the effective collective light-matter coupling $g\sqrt{N\tau'} > \{\gamma^z, \gamma^-, \kappa\}$, dominates over the decay channels. In this regime, the time scale of cavity dynamics is fast relative to the decay rate, and we observe $\sqrt{N}$-superextensive power scaling and $1/\sqrt{N}$ dependence of rise time, while the maximum energy density remains constant. While power scaling is superextensive in both regimes, the origin of this differs: for the decay-dominated regime this is the result of the superextensive energy scaling, while for the coupling-dominant regime it is the result of a superextensive decrease in the rise time. Experiments A1 and A2 operates in this regime (Fig. 3a).

In the crossover between the regimes (purple-green), the collective coupling falls between the cavity decay rate and the TLS dephasing rate, $\{\kappa, \gamma^-\} < g\sqrt{N\tau'} < \gamma^z$. In Fig. 3a and b, $\gamma^-$ is small such that $g\sqrt{N\tau'} \gg \gamma^-$ for all values of $N$, and so there is no boundary labelled for this decay rate. In this case, capacity and rise-time can simultaneously scale super- and subextensively, but at a rate slower than in the decay and coupling-dominated regimes, respectively. Experiments B1 and B2 operate in this regime (Fig. 3b).

**Decay and coupling rates**

The parameters needed in the theory calculations are the cavity leakage rate $\kappa$, the dephasing rate $\gamma^z$, the non-radiative decay rate $\gamma^-$, the interaction strength $g$, and the
temporal width of the instrument response function, $\sigma_R$. Note that the temporal width of
the pump pulse is fixed at $\sigma = 20$ fs. Using transfer matrix modelling on the weakly
coupled cavities we estimate that the cavity leakage rate $\kappa$ is around 2.1 and 2.2 meV for
the 1% and 0.5% cavities respectively. Consistent with this, we used $\kappa = 2$ meV in the
theory calculations for all cavities. Based on the measured finesse of the cavities we
estimate that $\sigma_R = 120$ fs, which we then use in all theory calculations. For the dephasing
rate, we note that as one enters the strong-coupling regime, exciton delocalisation
suppresses the effect of dephasing\textsuperscript{37}. To approximately capture this effect, we assume that
the dephasing rate scales with the number of molecules as $\gamma^z = \gamma^z_0 \left( \frac{N_{5\%}}{N} \right)$ where $\gamma^z_0$ is
taken to be constant and $N_{5\%}$ is the number of molecules in the 5% cavity. The
experimental uncertainty in $N$ is estimated to be 10%.

The remaining three parameters in the model ($\gamma^z_0$, $\gamma^-$, and $g$) were found through
a global chi-squared optimisation, simultaneously optimising over all experiments.
Uncertainties in these fitting parameters were then estimated by using the reduced $\tilde{\chi}^2$
distribution to find the 68% confidence interval of the model parameters. This
corresponds to the range $\tilde{\chi}^2 \leq \tilde{\chi}^2_{\text{min}} + \Delta$, where for a three parameter optimisation and
$k$ total data points $\Delta \approx 3.51/(k - 3)$\textsuperscript{38}. From this procedure we found $\gamma^- = (0.0263^{+0.0031}_{-0.0030})$ meV, $\ g = (16.1^{+1.0}_{-1.3})$ neV and $\gamma^z_0 = (1.41^{+0.19}_{-0.17})$ meV. See
Supplementary Information for more details.

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Extended Data Figures

Extended Data Figure 1: Photoluminescence quantum yield as function of LFO concentration.
Extended Data Figure 3: Absorption, photoluminescence of the LFO films and reflectivity spectra of the quantum battery microcavities. (a) Absorption and (b) photoluminescence spectra for the 0.5%, 1%, 5%, and 10% LFO-concentration films. (c) Reflectivity spectra for
0.5%, 1%, 5%, and 10% LFO-concentration microcavities. UPB, MPB, and LPB label the upper, middle, and lower polariton branches, respectively. Also indicated are the 0-0 and 0-1 transition wavelengths. (d) is a slice of the reflectivity spectra at 37°. The single dip in the 0.5% and 1% concentration spectra indicate the weak-coupling regime. The double dip seen in the 10% concentration spectra, represent the polaritonic states, indicating the strong-coupling regime. The 5% concentration spectrum represents a situation intermediate between a single and double dip, indicating an intermediate-coupling regime.
Extended Data Figure 2: Energetics of the quantum batteries without convolution by the instrument response function.
Extended Data Figure 4: Transfer matrix simulation of the electric field distribution for the 1% cavity. (a) shows the cavity reflectivity, (b) the spectrally-resolved electric field amplitude, and (c) the electric field amplitude at the cavity mode wavelength. The shaded sections of (c) indicate the different materials which make up the cavity, with Nb$_2$O$_5$ in purple (refractive index, n = 2.25), SiO$_2$ in blue (n = 1.52), and LFO in PS in orange (n = 1.60). All simulations were made using transfer matrix modelling at an angle of 20° to the cavity normal to maintain consistency with the transient reflectivity measurements.
### Extended Data Table 1: Summary of the experimental results

In experimental groupings A1, A2, A3 and B1, B2, the number of molecules \( N \) increase whilst the ratio of photons to molecules remains constant \( (r \approx 0.14 \text{ and } 2.4 \text{ respectively}) \). The rise time \( \tau \), is the time to reach \( E_{\text{max}}/2 \). The battery capacity \( E_{\text{max}} \), is the peak stored energy per molecule or energy density. The battery charging rate \( P_{\text{max}} = \max (dE / dt) \), is the peak charging power per molecule or charging power density.

| Exp. | \( N \times 10^{10} \) | \( \tau \) [ps] | \( E_{\text{max}} \) [eV] | \( P_{\text{max}} \) [eV/ps] |
|------|----------------|----------------|----------------|----------------|
| A1   | 16             | 0.08           | 0.20           | 1.94           |
| A2   | 8.1            | 0.11           | 0.19           | 1.20           |
| A3   | 1.6            | 0.21           | 0.07           | 0.21           |
| B1   | 1.6            | 0.16           | 0.83           | 3.31           |
| B2   | 0.8            | 0.21           | 0.25           | 0.75           |
Author contribution statement

J.Q.Q. conceived and managed the project. K.E.M and D.G.L. contributed to the fabrication of the DQBs. L.G, K.E.M., G.C. and T.V. contributed to the measurement of the DQBs. D.M.R, J.Q.Q., B.W.L, E.M.G. and J.K. contributed to the theoretical analysis. All authors contributed to discussion of the results and the writing of the manuscript.

Data availability

The datasets that support this work are available upon request from the corresponding authors.

Code availability

The codes used for analysis are available upon request from the corresponding authors.
S1. CUMULANT EQUATIONS

Here we derive the equations of motion for the expectation values using a second-order cumulant approach. As discussed in the main text, for $N$ identical molecules of energy $\omega_n$, the energy density of the quantum battery is

$$E(t) = \frac{\omega_n}{2} (\langle \sigma_z(t) \rangle + 1) ,$$

where $\langle \sigma_z(t) \rangle$ is the expectation value of any one of the $N$ molecules, which are all assumed identical. The system, comprising the molecules and the cavity mode, evolves under the master equation written in the main text, reproduced here ($\hbar = 1$):

$$\dot{\rho} = -i[H, \rho] + \kappa L[a] + \sum_{j=1}^{N} \left( \gamma^+ L[\sigma_j^+] + \gamma^- L[\sigma_j^-] \right) ,$$

$$H = \Delta a^+ a + \sum_{j=1}^{N} \left[ \frac{\Delta}{2} \sigma_j^z + g(a^+ \sigma_j^- + a \sigma_j^+) \right] + i\eta(t)(a^+ - a) ,$$

where $a$ ($a^+$) is the photon annihilation (creation) operator, $\sigma_j^\alpha$ for $\alpha = x, y, z$ are the Pauli matrices, $\Delta$ is the energy detuning of the laser from the cavity and molecules (set to 0), $g$ is the coupling strength of each molecule to the photon mode, $\eta(t)$ is the Gaussian profile of the pump laser and $\kappa, \gamma^+$ and $\gamma^-$ are the cavity leakage, dephasing and non-radiative decay rates.

To determine the time evolution of $\langle \sigma_z(t) \rangle = \text{Tr} [\sigma_z \rho(t)]$ we begin by writing down the first order expectation values of the system. We adopt the notation $C_{\alpha}(t) \equiv \langle a(t) \rangle$ for photon operators, and $C_{\alpha=x,y,z}(t) \equiv \langle \sigma_\alpha(t) \rangle$ for spin operators, along with a similar notation for higher order expectations, e.g., $C_{\alpha x}(t) \equiv \langle a \sigma_x(t) \rangle$. The equations of motion for the first order expectation values are

$$\partial_t C_a = - (i\Delta_x + \frac{1}{2} \kappa) C_a - \frac{1}{2} g N \langle iC_x + C_y \rangle + \eta(t) ,$$

$$\partial_t C_x = - \Delta_x C_y - 2g \text{Im} [C_{az}] - \gamma^{tot} C_x ,$$

$$\partial_t C_y = \Delta_x C_x - 2g \text{Re} [C_{az}] - \gamma^{tot} C_y ,$$

$$\partial_t C_z = 2g (\text{Re} [C_{ay}] + \text{Im} [C_{az}]) - \gamma^- (C_z + 1) ,$$

where $\partial_t$ is short for $\frac{\partial}{\partial t}$, $\gamma^{tot} = 2\gamma^+ + \frac{1}{2} \gamma^-$, and for notational ease we have dropped the explicit time dependence of observables. As described in the main text, in mean field theory we would now set the second
order cumulants to zero. These are defined as

\[ \langle \langle AB \rangle \rangle = \langle AB \rangle - \langle A \rangle \langle B \rangle . \]  

(8)

This would result in the usual decomposition of second order expectation values into products of first order ones, \( C_{AB} = C_A C_B \), which is the assumption that molecule-molecule, molecule-photon, photon-photon and all higher order correlations are negligible. However, we instead derive equations of motion for the second order expectation values, capturing the leading order 1/N corrections to mean field theory. The second order photon correlations obey:

\[
\partial_t C_{a^1a} = -\kappa C_{a^1a} - gN (i \text{Im} [C_{ax}] + \text{Re} [C_{ay}]) + 2\eta(t) \text{Re} [C_a],
\]

(9)

\[
\partial_t C_{aa} = -(2i\Delta + \kappa) C_{aa} - gN (iC_{ax} + C_{ay}) + 2\eta(t)C_a,
\]

(10)

while molecule-photon correlations follow:

\[
\partial_t C_{ax} = -(i\Delta_c + \frac{1}{2}\kappa + \gamma^{tot}) C_{ax} - \Delta_a C_{ay} - i\frac{g}{2} [1 + (N - 1)] C_{xx}
\]

\[
- \frac{g}{2} [iC_{yz} + (N - 1) C_{zy}] + ig (C_{aa} - C_{a^1a}) + \eta(t)C_x,
\]

(11)

\[
\partial_t C_{ay} = -(i\Delta_c + \frac{1}{2}\kappa + \gamma^{tot}) C_{ay} + \Delta_a C_{ax} - i\frac{g}{2} [-iC_{z} + (N - 1) C_{xy}]
\]

\[
- \frac{g}{2} [1 + (N - 1) C_{yy}] - g (C_{aa} + C_{a^1a}) + \eta(t)C_y,
\]

(12)

\[
\partial_t C_{az} = -(i\Delta_c + \frac{1}{2}\kappa) C_{az} - \gamma^{-} (C_{az} + C_{a}) - \frac{g}{2} [-iC_{z} + (N - 1) C_{yz}]
\]

\[
- i\frac{g}{2} [iC_{yz} + (N - 1) C_{zy}] + g (C_{aa} + C_{a^1a}) - ig (C_{aa} - C_{a^1a}) + \eta(t)C_z .
\]

(13)

These now depend on third order expectation values, some of which contain multiple Pauli operators. We must note that these terms indicate Pauli operators representing different molecules and so commute — we have already taken into account the cases where the Pauli operators correspond to the same molecule by using the Pauli algebra \( \sigma^\alpha \sigma^\beta = \frac{1}{2} \delta^\alpha^\beta + i \sigma^\rho \epsilon^\alpha^\beta^\gamma \). The molecule-molecule expectation values for the same Pauli operator acting on different molecules are

\[
\partial_t C_{xx} = -2\Delta_a C_{xy} - 4g \text{Im} [C_{ax}] - 2\gamma^{tot} C_{xx},
\]

(14)

\[
\partial_t C_{yy} = 2\Delta_a C_{xy} - 4g \text{Re} [C_{ay}] - 2\gamma^{tot} C_{yy},
\]

(15)

\[
\partial_t C_{zz} = 4g (\text{Im} [C_{azz}] + \text{Re} [C_{ayy}]) - 2\gamma^{-} (C_{zz} + C_{z}) .
\]

(16)

Finally, the molecule-molecule expectation values for different Pauli operators acting on different molecules are

\[
\partial_t C_{xy} = \Delta_a (C_{xx} - C_{yy}) - 2g (\text{Re} [C_{ax}] + \text{Im} [C_{ay}]) - 2\gamma^{tot} C_{xy},
\]

(17)

\[
\partial_t C_{xz} = -\Delta_a C_{yz} + 2g (\text{Re} [C_{axy}] + \text{Im} [C_{azz}] - \gamma^{tot} C_{xz} - \gamma^{-} (C_{zz} + C_{z}) ,
\]

(18)

\[
\partial_t C_{yz} = \Delta_a C_{xz} + 2g (\text{Re} [C_{ayy}] - \text{Re} [C_{azz}] + \text{Im} [C_{axy}]) - \gamma^{tot} C_{yz} - \gamma^{-} (C_{yz} + C_{y}) .
\]

(19)

In principle one can continue to write equations of motion for increasingly higher orders of expectation values, however, at large \( N \), most essential physics is obtained at second order. We therefore truncate the cumulant expansion by setting third order cumulants to zero. These are defined as

\[
\langle \langle ABC \rangle \rangle = \langle ABC \rangle - \langle AB \rangle \langle C \rangle - \langle A \rangle \langle BC \rangle - \langle AC \rangle \langle B \rangle + 2 \langle A \rangle \langle B \rangle \langle C \rangle ,
\]

(20)

and so setting \( \langle \langle ABC \rangle \rangle = 0 \) closes the system of differential equations, allowing us to write \( \langle ABC \rangle \) in terms of first and second order correlations.
In Fig. S1 we present the theoretical $N$-dependence of the charging time $\tau$, maximum energy density $E_{\text{max}}$, and maximum power density $P_{\text{max}}$ over a wider range of $N$ than shown in Fig. 3 of the main text. This shows that in addition to the decay-dominated (purple) and coupling-dominated (green) behavior described in the main text, a third region occurs at even larger $N$, which we discuss below.

In the main text we discussed the QB energetic dynamics around the decay-to-coupling dominated crossover regime, as this was the experimental operating region. Moving deeper into coupling-dominated regime does not necessarily improve the battery operation. This is illustrated in Fig. S1(b) which shows the simulated four points, corresponding to the circles in Fig. S1(a). Within the coupling-dominated regime, energy stored within the battery rapidly oscillates which is not a desirable feature. This occurs because the light and matter degrees of freedom hybridise to form polaritons with upper and lower branches split by Rabi frequency $\pm g\sqrt{N}$, leading to beating between these modes. These oscillations are not present in the experimentally studied crossover region. In this region, dephasing is strong enough to prevent oscillation in energy, yet weak enough to warrant superextensive charging. Therefore, this is the optimal region to produce a QB. Going deeper into the coupling-dominated regime would only be advantageous if energy was extracted from the battery on a shorter timescale than the period of oscillations, or additional mechanisms were in place to stabilise the oscillations.

At even larger $N$ (red region) the stored energy falls with increasing $N$. This can be understood as arising from a condition where the polariton energy splitting exceeds the bandwidth of the pump (set by its finite pulse duration), suppressing energy absorption. Numerically, we find this occurs when $N > N_\sigma$ where $g\sqrt{N_\sigma} = (2/5)^{1/4}\sigma$, which signifies the onset of this non-resonant regime. The prefactor $(2/5)^{1/4}$ will be explained in Section S3. To build an efficient QB in this regime, one should tune the frequency of the laser to match the polariton energies. Additionally, the time dynamics of energy absorption here change significantly, with the second half of the laser pulse causing stimulated emission, reducing the stored energy — such dynamics arises naturally from a toy model of strongly coupled modes with a splitting larger than the pulse bandwidth, and can be seen in the form of the red line in Fig. S1(b).

**FIG. S1.** (a) Charging time, battery capacity and maximum power as a function of $N$. This figure is identical to Fig. 3(a) in the main text, but extended to larger range of $N$. At large $N$ the energy of the battery can reach half maximum before the laser pulse finishes, in which case the charging time $\tau$ becomes negative. (b) Examples of dynamics in each regime. The values of $N$ used in these dynamics corresponds to the circles of the same colour in (a).
S3. THE BOUNDARY BETWEEN DECAY AND COUPLING DOMINANT REGIMES

There are two timescales in this system: the vacuum Rabi splitting (i.e. polariton detuning) $g\sqrt{N}$ and the Rabi splitting $g\sqrt{rN}$ where $rN$ is the number of photons in the cavity. In Fig. 3(a), we show that the battery charges super-extensively once $g\sqrt{N}$ is greater than all decay channels. However, this is only true if $r \leq 1$, as is true in experiments A1, A2 and A3. In Fig. 3(b), the boundaries $N_\kappa$ and $N_\gamma$ are instead determined by $g\sqrt{rN}$ being equal to the decay rates. This is because $r \geq 1$ in experiments B1 and B2. More generally, the important timescale is the larger of the polariton detuning and the Rabi splitting, and so the coupling dominant regime occurs when $g\sqrt{\text{Max}(1,r)N}$ is larger than all decay channels.

In Figure S2 we plot the charging time $\tau$ as a function of $N$ and $r$. Here, we set $\kappa = \gamma^- = \gamma^z = \Gamma = 2$ meV (note that $\gamma^z$ is independent of $N$) so that there is only one boundary between the decay dominant and coupling dominant regimes. The green, red and dashed-black lines show the boundaries between the decay dominant and coupling dominant regimes ($N = N_\Gamma$) if $g\sqrt{N}$, $g\sqrt{rN}$ or $g\sqrt{\text{Max}(1,r)N}$ are used as the relevant coupling scale respectively. Clearly, the boundary is determined by $g\sqrt{\text{Max}(1,r)N}$ for all values of $r$. We also show the boundary between the coupling dominant and non-resonant regimes ($N = N_\sigma$) as the cyan line. When $r > 1$, we find that $N_\sigma$ becomes linearly dependent on $r$. The prefactor $(2/5)^{1/4}$ is necessary for $N_\sigma$ to align with the contours of increased charging time for $r > 1$.

![Figure S2](image-url)  

**FIG. S2.** The charging time of the battery as a function of number of molecules $N$ and laser intensity $r$. All parameters are equivalent to the Q1% cavity (see main text) with the exception that the dephasing and non-radiative decay rates are equal to the cavity leakage rate (set to $\gamma^- = \kappa = \Gamma = 2$ meV) and note that the dephasing rate is independent of $N$. 


S4. DEPENDENCE ON LASER INTENSITY

Figure S3 shows how capacity, charging time and power vary as a function of laser intensity $r$ at fixed number of molecules $N$. For small $r$, we find that the maximum energy and power densities vary linearly with $r$, while charging time is constant. This simply reflects the total energy in the cavity. The charging time is constant because decay channels still dominate over coherent dynamics. As $r$ is increased beyond $r = 1$, the important timescale $g \sqrt{\max(1,r)N}$ begins to scale with $r$, and so the boundaries separating the coupling dominant and decay dominant regions $N_k$ and $N_{\gamma z}$ are pushed to smaller $N$. When these boundaries become smaller than the number of molecules in the cavity, the charging time begins to scale as $1/\sqrt{r}$. Additionally, the energy density begins to saturate because there are already many more photons than there are molecules within the cavity. In Figure S3(b) we also plot the experimentally measured energy densities, and we see there is good agreement to the theoretical curve. The coloured points in Figure S3(a) indicate the charging time, maximum capacity and maximum power of the temporal dynamics of the same colour in Figure S3(b).

FIG. S3. Behavior vs pump intensity $r$. (a) Capacity, charging time and maximum power vs $r$ for a fixed number of molecules $N = 1.62 \times 10^{19}$ (the 1% cavity). All other parameters align with those used to model the 1% cavity. (b) Comparison of theoretical and experimental charging dynamics for four values of $r$. These are indicated by circles in the charging time panel of (a), showing the experimentally measured values.
S5. FITTING OF MODEL PARAMETERS

As outlined in the main text, we used a reduced chi-square optimisation procedure to determine the light matter coupling \( g \), dephasing constant \( \gamma_0 \) and non-radiative decay rate \( \gamma^- \), as well as to estimate uncertainties on these parameters. As these quantities represent molecular properties, we would expect them to be the same in all the different experiments. For this reason, we performed a global fit rather than performing the procedure individually for each experiment. In this section we give further details on this calculation.

A. Fitting procedure

The steps of our fitting procedure are as follows:

1. Calculate the theoretical \( E(t) \) curves for a grid of parameter values \( g, \gamma^z, \gamma^- \), along with the values of \( N \) relevant for all five experiments, A1, A2, A3, B1 and B2. Based on previous observations, we chose the search region of the parameter space as \( g \in [0.1, 5000] \) neV; \( \gamma^z_0 \in [0.1, 5000] \) meV and \( \gamma^- = [0.001, 1] \) meV. Subsequent refinements of this search region were made to give higher resolution near the optimal point.

2. We estimate uncertainties, \( \sigma_i \) on each experimental data point (transient reflectivity vs time), by considering the point-to-point variation. Because the uncertainty is higher near \( t = 0 \), when the pump arrives, we use different error estimates in different time windows. Specifically, we divide experiments A1 and A2 into five windows \( t < -300fs; -300fs < t < 300fs; 300fs < t < 700fs; 700fs < t < 1000fs; t > 1000fs \). For experiments A3, B1 and B2 we found that four windows \( t < -300fs; -300fs < t < 300fs; 300fs < t < 1000fs; t > 1000fs \) was sufficient. In each window, the uncertainty estimate for each experiment is taken from the variance over a narrow range of points (typically 150fs) where there is no strong time dependence.

3. For each set of parameters, we performed an “internal” chi-square minimisation to find the optimal scaling factor \( S \) between the battery energy \( E(t) \) and the measured differential reflectivity \( \Delta R/R \), and a time shift between the theory and experiment \( T_0 \). That is, we minimise

\[
\chi^2 = \sum_i \left( \frac{S \times (\Delta R/R)_i - E(t_i + T_0)}{\sigma_i} \right)^2,
\]

with respect to \( S \) and \( T_0 \). We treat the result of this minimisation as the chi-squared value which we use in the following steps to estimate the meaningful parameters \( g, \gamma^z, \gamma^- \) and their uncertainties.

Estimating the scaling factor \( S \) from first principles is difficult because of reflections by the cavity mirror, hence this factor is found by the best fit value. The time shift reflects uncertainty of delays in the optics, so that it is not a-prior clear when the peak of the pump pulse arrives. After this shift, we define \( t = 0 \) as the moment the pump arrives. This is important when calculating the charging time \( \tau \), which we defined as the time from the arrival of the pump until the battery reaches half maximum energy.

4. We then use the chi-square value described above, and divide by the total number of degrees of freedom \( k_{\text{eff}} = k - 3 \) (where \( k \) is the total number of data points), to arrive at the final reduced chi-square \( \tilde{\chi}^2 \) map. A slice of this three dimensional reduced chi-square map is shown in Figure S4 for \( \gamma^- = 0.0263 \) meV, which is the optimal non-radiative decay rate given in the main text. The optimal parameter set used in the main text that optimises \( \tilde{\chi}^2 \) is shown as the red point in Figure S4. We find \( \tilde{\chi}^2_{\text{min}} = 2.76 \), suggesting our estimated measurement uncertainties on \( \tilde{\chi} \) are reasonable, but likely underestimates.

5. Finally, the 68% confidence interval for each parameter was estimated by considering the contour for which \( \tilde{\chi}^2 = \tilde{\chi}^2_{\text{min}} + \frac{1}{2} k_{\text{eff}} \Delta^* \) where \( \Delta^* = 3.51 \) is extracted from the reduced chi-square distribution for 3 parameters and error tolerance (68%), see [1]. In the right panel of Fig. S4 we show the contour as a white line, and the actual parameter values which lie within this 68% contour as black points.
FIG. S4. An illustration of the reduced-chi square optimisation procedure to find the optimal parameters for the theoretical model and their 68% confidence intervals, where $\Delta = \Delta^*/k_{\text{eff}}$. The chi-square contour plots shown in this figure are slices of the full three-dimensional map at the optimum non-radiative decay rate $\gamma^- = 0.0263$ meV used in the main text. In the yellow region of the bottom right corner $\chi^2 > 10$, which we do not show to emphasise smaller variations in $\chi^2$.

### B. Residuals of the best fit

To check whether systematic errors arise from our fitting procedure, Fig. S5 shows the residual errors—i.e. difference between the theoretical curves and the experimental data—for the five experiments shown in Figure 2 of the main text. As is clear, there are no discernible features in the residuals that are consistently present across the different experiments. This indicates that the theoretical curves account for the essential characteristics of the data.

FIG. S5. The residuals of the theoretical curves and the experimental data over the duration of the experiments.

[1] Jasper Vivian Wall and Charles R Jenkins. *Practical statistics for astronomers*. Cambridge University Press, Cambridge, 2012.