

Extending the Self-Discharge Time of Dicke Quantum Batteries Using Molecular Triplets

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Quantum batteries, quantum systems for energy storage, have gained interest due to their potential scalable charging power density. A quantum battery proposal based on the Dicke model has been explored using organic microcavities, which enable a cavity-enhanced energy-transfer process called superabsorption. However, energy-storage lifetime in these devices is limited by fast radiative emission losses, worsened by superradiance. Here, we demonstrate a promising approach to extend the energy-storage lifetime of Dicke quantum batteries using molecular triplet states. We examine a type of multilayer microcavity where an active absorption layer transfers energy to the molecular triplets of a storage layer, identifying two regimes based on exciton-polariton resonances. We tested one of these mechanisms by fabricating and characterizing five devices across a triplet-polariton resonance, showing that triplet population is maximized when the lower polariton and triplet state are isoenergetic. We found that one of these devices can store energy for $40.3 \pm 0.4 \mu\text{s}$, a 10^3 -fold increase in storage time compared to previous demonstrations. We conclude by discussing potential optimization outlooks for this class of devices.

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I. INTRODUCTION

Batteries, now a crucial element in a wide range of energy-efficient applications, are being seamlessly integrated into smart electronics, textiles, the Internet of Things, and electric vehicles, thereby reshaping our way of life. Large-scale battery-based energy storage is proving instrumental in addressing intermittency challenges associated with renewable energy sources, such as solar and wind power [1]. However, the current generation of electrochemical batteries, especially Li-ion ones, are largely deficient in their ability to charge quickly and efficiently; they suffer from rapid degradation and require replacement after only a few hundred cycles [2]. Consequently, the advent of novel energy-storage technologies (beyond electrochemistry) with fast charging while maintaining high energy density is urgently required [3].

In a quantum battery (QB), a theoretical construct for energy storage, energy is stored in the excited states of a quantum system, such as atoms or molecules, and can be extracted by inducing transitions between these states. Conceptually, QBs aim to harness properties like superposition and quantum entanglement to achieve an advantage for energy storage: similarly to Grover’s search algorithm for quantum computing [4], quantum batteries can offer a $\sqrt{N}$ -fold charging speedup that grows with the number N of subcells involved [5]. The nature of such speedups can either be linked to entanglement generation [6,7], coherent processes [8], or collective dynamics [9], as discussed in depth in Refs. [5,9,10].

A promising architecture to achieve superextensive charging power is the *Dicke quantum battery*, proposed by Ferraro *et al.* [11], which is based on the Dicke model of light-matter interaction between an optical cavity and a set of N (noninteracting) emitters [12–14]. Ferraro *et al.* [11] theoretically demonstrated that by leveraging a phenomenon known as *superabsorption* a Dicke battery’s charging power density could reach the $\sqrt{N}$ charging speedup [15–19]. A significant breakthrough was achieved with the recent experimental demonstration of superabsorption on an organic optical microcavity [20]. The results suggest that the energy-transfer rate from the optical cavity

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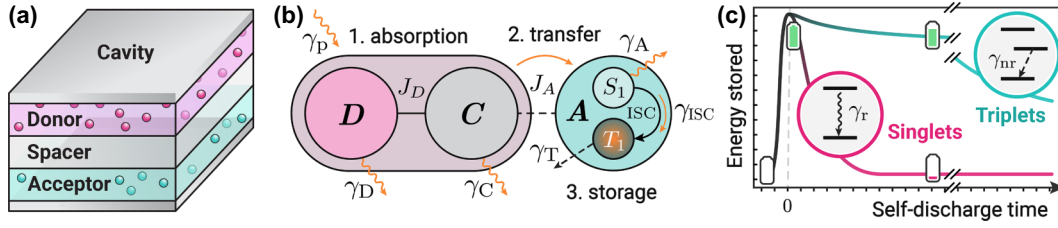


FIG. 1. Storage layer in a Dicke exciton-polariton quantum battery. (a) We consider a microcavity with a donor and acceptor layer, separated by an inert polymer spacer to avoid direct dipole-dipole couplings between them. The donor is chosen to be a bright, strongly absorbing dye, while the acceptor is chosen to absorb weakly and to have a dark molecular triplet state. (b) We use an effective Jaynes-Cummings model, shown in Eq. (1), describing the optoelectronic properties of the devices, consisting of a cavity (C) strongly coupled to the donor’s singlet (D) via J_D and weakly coupled to the acceptor’s singlet (S_1 at A) via J_A . The acceptor’s triplet state (T_1 at A) can be populated via intersystem crossing (ISC) from its singlet (S_1) or optically via weak dipole-dipole couplings. (c) By transferring energy to the dark molecular triplet states of the acceptor layer we aim to prevent the detrimental effects of superradiance, i.e., the counterpart of superabsorption, which leads to short self-discharge time due to cavity-enhanced radiative emission losses from the bright donor singlets, usually in the pico to nanosecond timescale. Instead, the triplets’ lifetime can be orders of magnitude longer, leading to microsecond self-discharge times.

mode to the photoactive molecules in the microcavity (analogous to a battery-charging speed), increases superextensively with the number of molecules, thereby supporting the superabsorption hypothesis, i.e., devices charge faster as their storage capacity increases.

Superabsorption, however, is a double-edged sword. While it enables ultrafast charging, i.e., the transfer of energy from the cavity to the emitters, it also introduces its well-known counterpart, *superradiance*, which results in a cavity-enhanced relaxation pathway, leading to fast battery discharge [21–30]. Although superradiance can be partially offset by local decoherence [20], the natural radiative emission rate of individual emitters (typically nanoseconds) sets an upper limit on the storage time of that version of a Dicke QB. Indeed, the first experimental realization of this system by Quach *et al.* [20] observed extremely brief self-discharge times (nanoseconds). Therefore, a challenge in this research area is to discover strategies to prolong the storage lifetime of such devices, a critical prerequisite for their prospective application in energy storage.

Here we propose a Dicke QB architecture where superextensive absorption is spatially decoupled to energy storage within the same device. To achieve this, the devices consist of donor and acceptor layers, shown in Fig. 1(a), the former responsible for superabsorption while the latter has a built-in mechanism that permits prolonged energy storage. As an embodiment of the concept, the acceptor layer we study in this letter stores energy using molecular triplet states (or triplet *excitons*). As illustrated in Fig. 1(b), molecular triplet states (T_1) are typically orders of magnitude darker than the bright singlet states (S_1), while being only slightly less energetic, thus offering a promising approach to counter the *detailed balance* imposed by the superabsorption-superradiance “duality.” While dark electronic states have been considered to reduce losses in energy harvesting [31,32], exciton transport [33,34], and energy storage [35,36], so far, dark states have been

produced mostly through superpositions of locally bright states (e.g., the ground states of H aggregates [37]). These, however, tend to be sensitive to local disorder and decoherence that perturb the symmetry required to cancel out optical dipole moments [35]. Here, instead, we focus on molecular triplet states, which are naturally prohibited to relax via radiative emission due to spin-forbidden transitions [38], leading to exciton lifetimes that span from microseconds to minutes [39], and therefore longer-energy storage times in QBs [Fig. 1(c)].

To this end, we propose a proof-of-concept device as a Dicke QB model system based on a multilayer optical microcavity, inspired by the work of Zhong *et al.* [40] and schematically shown in Fig. 1, wherein the interaction between the electromagnetic mode of the cavity and a “donor” layer ensures superabsorption (i.e., fast battery charging) as experimentally demonstrated by Quach *et al.* [20]. The absorbed energy is transferred into an acceptor *storage layer* comprised of molecular species with efficient intersystem crossing and with long-lived triplet states, therefore preventing superradiant battery discharge.

Using an approximate theoretical model [Eq. (1)], we show two possible pathways for energy storage in our architecture, both mediated by resonance conditions and characterized by widely different optoelectronic and energy-storage properties. We experimentally realize devices exhibiting one such mechanism and show that energy is stored for tens of microseconds, a 10^3 -fold increase in storage time compared to previous demonstrations [20].

II. DEVICE DESIGN AND MODELING

We use the effective Jaynes-Cummings Hamiltonian of Eq. (1) associated with the underlying many-body Dicke model [41–44] to find key experimental conditions that result in enhanced efficiencies of energy transfer from

TABLE I. Model parameters for each device, obtained using Eq. (1).

Jaynes-Cummings model device parameters				
	ω_C (eV)	J_D (eV)	J_A (eV)	ΔE (eV)
Cavity 1	2.12	0.23	0.07	0.216
Cavity 2	1.97	0.23	0.10	0.094
Cavity 3	1.89	0.23	0.07	0.036
Cavity 4	1.88	0.25	0.08	0.011
Cavity 5	1.79	0.27	0.13	-0.091

an external driving field—such as a cw laser—to the energy-storage layer of the device shown in Fig. 1.

In the rotating-wave approximation [45], this Hamiltonian reads

$$H = \omega_C(\theta)a^\dagger a + \sum_{v=D,A} \left\{ \omega_v \sigma_+^{(v)} \sigma_-^{(v)} + J_v (\sigma_+^{(v)} a + \sigma_-^{(v)} a^\dagger) \right\}, \quad (1)$$

where the cavity mode has an energy $\omega_C(\theta)$ that depends on the angle of incidence of light θ [44] (note that for shorthand notation we have set $\hbar = 1$). $J_D = \sum_{j=1}^{N_D} g_D^{(j)}$ ($J_A = \sum_{j=1}^{N_A} g_A^{(j)}$) is the cumulative coupling between cavity and donor (acceptor), ω_D (ω_A) is the average energy [46] of the molecules in the donor (acceptor) layer, a , $a^\dagger$ are the annihilation and creation operators of the cavity and $\sigma_\pm^{(v)} = \sigma_x^{(v)} \pm i\sigma_y^{(v)}$ are the singlet-exciton creation and annihilation operator at chromophore $v = D, A$. The acceptor A is a three-level system with a triplet state T . The latter may have a small residual optical dipole moment, which leads to a cavity-triplet coupling with strength J_T . We use Eq. (1) to obtain the model parameters presented in Table I, associated with each device shown in Fig. 3.

Note that all incoherent transitions, such as radiative and nonradiative emission losses are modeled using the following Lindblad, Markovian quantum master equation:

$$\dot{\rho} = -\frac{i}{\hbar}[H, \rho] + \sum_k \gamma_k \left(L_k \rho L_k^\dagger - \frac{1}{2} \{ L_k^\dagger L_k, \rho \} \right), \quad (2)$$

where L_k are incoherent transition operators with associated rates γ_k . The incoherent transitions that we model include the laser pumping rate γ_p , cavity loss rate γ_C , singlet exciton radiative emission rates γ_D , γ_A for donor and acceptor, respectively, triplet nonradiative decay γ_T , and intersystem crossing (ISC) rate γ_{ISC} for the $S_1 \rightarrow T_1$ transition at the acceptor (see Supplemental Material [47]).

The strong interaction between the optical cavity mode and the excited (singlet) states of the D and A materials results in the formation of polariton states [48]. In our model, we consider cases where the cavity-donor interaction strength greatly surpasses the equivalent cavity-acceptor coupling. In turn, this translates into *upper*

(UP) and *lower* (LP) polaritons with strong cavity-donor hybridization, and *middle polaritons* (MP) with nearly 100% acceptor character. Our model allows us to monitor the impact of parameters that can be experimentally manipulated on the population of triplet states. This, in turn, enables us to optimize energy storage. We now discuss the two main mechanisms that allow for energy transfer to the storage layer of the considered devices (Fig. 2).

A. Mechanism 1: ISC-mediated transfer at polariton-acceptor (singlet) resonance

In this mechanism, the device is expected to be superextensively charged due to the collective and synchronized interaction between the cavity mode and the donor singlet states. Energy is transferred to the acceptor singlet states whenever a resonance condition occurs between the acceptor singlets and a cavity-donor polariton, as shown in Fig. 2(a). Fast ISC populates the triplet states of the storage layer, which are assumed to have a negligible optical dipole moment and are consequently completely dark.

Mechanism 1 is efficient if: (i) the ISC rate γ_{ISC} is comparable to or faster than the energy loss rates of the QB (in turn dictated by an interplay of singlet donor γ_D acceptor γ_A and cavity photon γ_C decay rates) and (ii) a resonance condition occurs between the acceptor singlets and a cavity-donor polariton, such as the UP state shown in Fig. 2(a), or equivalently whenever:

$$\gamma_{ISC} > \gamma_C, \gamma_D, \gamma_A, \quad (3)$$

$$\omega_A \approx E_k, \quad (4)$$

where E_k is the energy of a (bright) polariton state of the QB (see Fig. 2(a), $k = \text{UP, LP, or MP}$). These conditions can be met by a careful choice of materials, where we note that ISC can be ultrafast in some compounds [49–51]. In this mechanism, the triplet states do not mix with singlets or cavity photons, and consequently, their lifetime remains unchanged and the time scale is set for energy storage (Fig. 2).

B. Mechanism 2: Optically driven transfer at polariton-triplet resonance

Following superextensive absorption by the donor layer in the device, energy can be directly transferred to the triplet states of the storage layer whenever one of the polariton states is resonant with the triplet state, and these states have a non-negligible *singlet character*. In layers with moderate to high dye concentration, random molecular aggregation can lead to triplets with singlet character [52–54], namely, with an effective overall spin-0 and a nonvanishing dipole moment. This leads to triplets that can interact with the cavity via a small dipolar coupling $J_T \ll J_D, J_A$, and can therefore be populated directly via

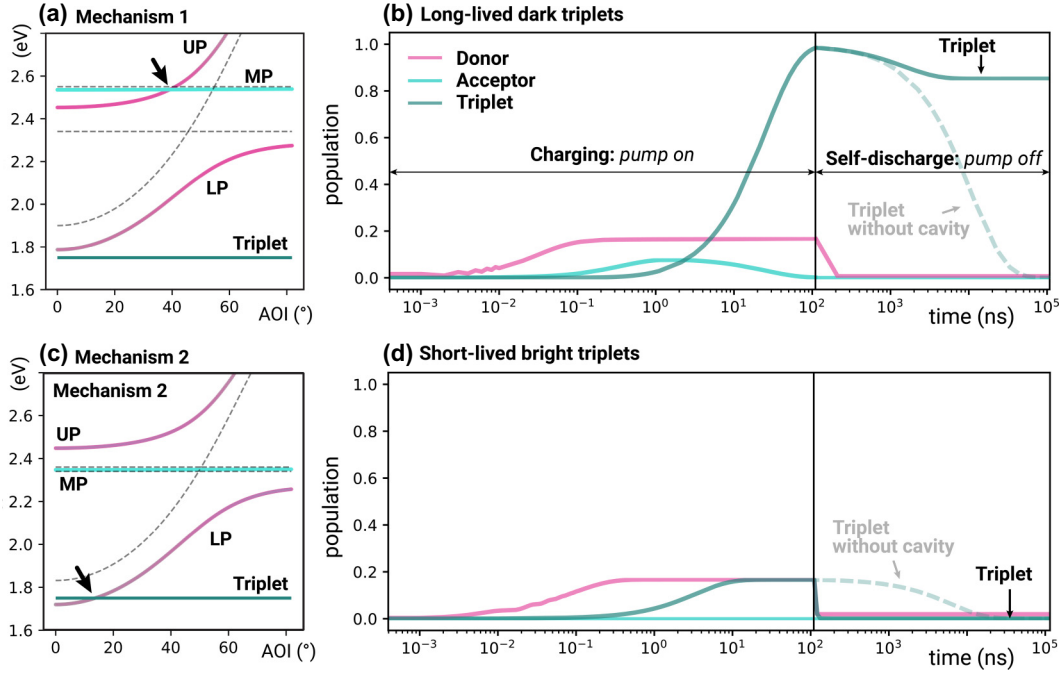


FIG. 2. Energy-storage mechanisms. Polaritons of the effective Jaynes-Cummings Hamiltonian of Eq. (1) and the acceptor’s triplet. The colors schematically represent the relative population of each diabatic state, with the middle polariton (MP) being predominately populated by the acceptor’s singlet. (a) Dark triplets can form via ISC at the resonance between the uncoupled acceptor’s singlet (gray dashed lines) and a bright highly absorbing polariton (here the “upper” polariton, which is a cavity-donor hybrid). In this case the molecular triplets are off resonance and do not couple with any other state. The triplets formed this way are dark and long lived. (b) Bright triplets can form via direct dipole-dipole coupling with a resonant bright polariton (here the “lower” polariton LP). The resulting triplets are hybrids (coherently mixed with the polariton state), therefore their lifetime is shortened by radiative recombination. The system parameters used to generate these figures are reported in the Supplemental Material [47]. (c) Mechanism 1 (top). The triplets formed in this case cannot fully decay via IC. A significant portion of the triplet remains populated indefinitely in the absence of additional relaxation pathways, leading to excellent energy-storage performance. (d) Mechanism 2 (Bottom). The bright hybrid triplets formed this way decay as fast as the cavity-donor polaritons, leading to poor energy-storage performance.

a polariton-triplet resonance. The resulting triplet states $\tilde{T}$ can form via coherent mixing between the bare acceptor triplets and the cavity-donor polariton, therefore their lifetime $\tau_{\tilde{T}}$ is shorter than the bare triplet lifetime $\tau_T = \gamma_T^{-1}$, and is approximately given by

$$\tau_{\tilde{T}} \approx p_T \tau_T + p_P \tau_P, \quad (5)$$

where p_T and p_P are the populations of the bare triplet and polariton states, respectively, and τ_P is the lifetime of the polariton state in resonance with the triplet state.

III. RESULTS

To explore the potential of the triplet storage layer, we fabricated five devices via thin film deposition, as detailed in the Supplemental Material [47].

We chose *Rhodamine 6G* (R6G) for the donor layer due to its robust optical absorption in the visible range, and small ISC quantum yield ($< 10^{-2}$) [55] while the acceptor layer is made of *Palladium tetraphenylporphyrin* (PdTPP), due to its efficient ISC to its molecular triplet

state (ISC quantum yield: 0.96 ± 0.04 [56]) and weak visible absorption (at its Q band). We designed the total distance L between the Ag mirrors to generate a second-order Fabry-Pérot cavity mode with antinodes at the locations of the D and A layers. The energy difference ΔE between the LP and the triplet state defines the detuning ΔE of the microcavity, $\Delta E = E_{LP} - E_T$, associated Jaynes-Cummings model parameters are summarised in Table I. In our experiments, we monitor the energy storage of each device by measuring their steady state and time-resolved fluorescence and phosphorescence, where the latter is directly correlated with the population of triplet states in the storage layer.

A. Steady-state emission

As shown through angle-dependent reflectometry in Fig. 3, our devices operate in the strong light-matter coupling regime, as evidenced by the anticrossing of the absorption bands around the intersection of exciton and cavity energies. These avoided crossings were accurately described with a three-level coupled oscillator model

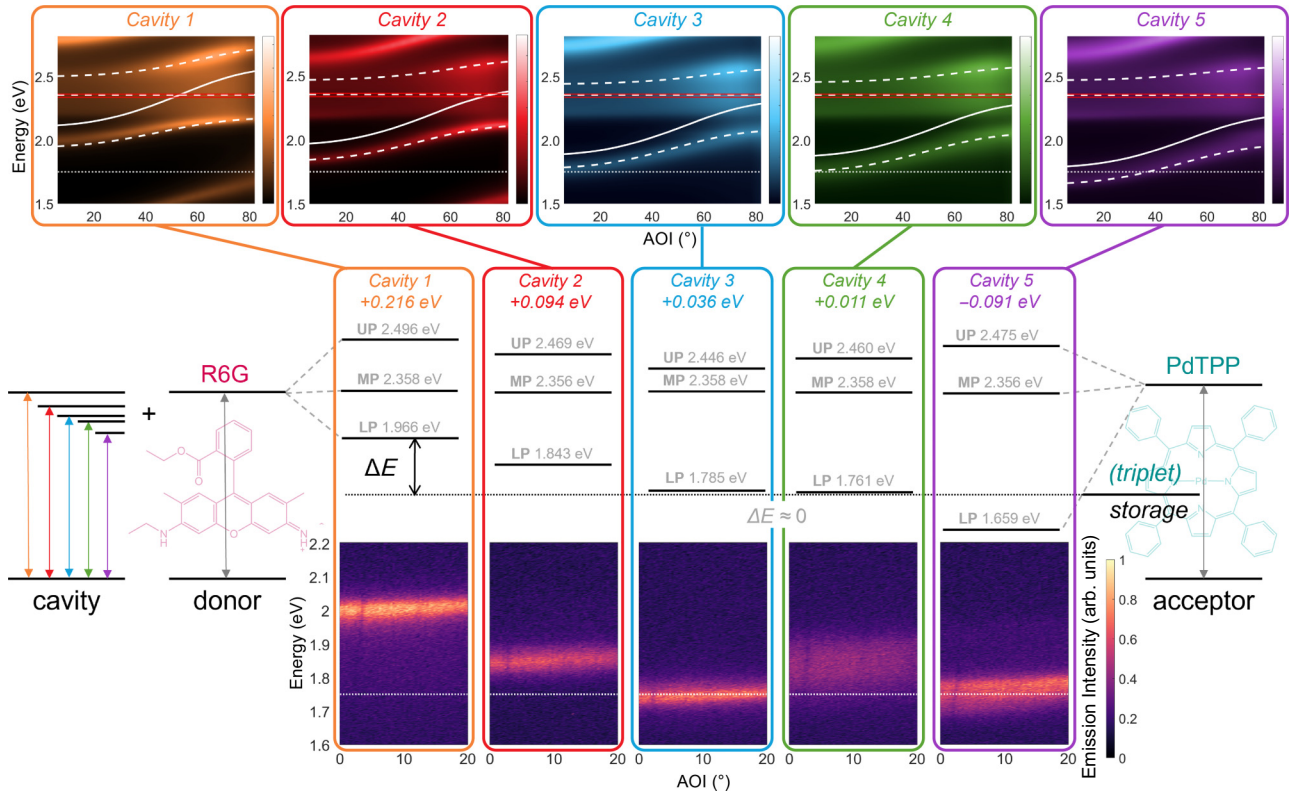


FIG. 3. Fluorescence emission properties across the LP-triplet resonance. Energy diagram outlining cavity detuning across the devices, with respective polariton energies from the effective Jaynes-Cummings model of Eq. (1), labeled upper (UP), middle (MP), and lower (LP) polariton. Fluorescence emission dispersions are normalized to cavity 1. As $\Delta E \rightarrow 0$, emission intensity is reduced and its features broaden about the triplet energy (white dashed line), exemplified in cavity 4. We attribute this to an increase in the population of the triplet state due to the optically driven mechanism, resulting in reduced brightness in the device. Angle-resolved absorption measurements of each device are included above, color coded to their respective device, where dashed white lines indicate polariton energies, solid white lines indicate cavity-mode energy, solid red lines indicate charging and storage layer singlet energies and dotted white lines indicate triplet storage energy.

(details in the Supplemental Material [47]), resulting in the set of parameters shown in Table I.

Figure 3 also shows how the emission of light from the devices (in turn related to their “charging state”) is affected by ΔE . In these measurements, the devices were illuminated using 514-nm cw laser irradiation at approximately $1.6 \mu\text{W}$, and the emission spectra were measured as a function of the angle relative to the surface normal of each device.

For cavity 1 and cavity 2, light is emitted at the spectral location of the LP band with a dependence on the angle that matches the one observed for absorption. This, together with the absence of clear triplet emission, indicates minimal energy transfer from the LP to the triplet at these ΔE values. In the isoenergetic ($\Delta E \approx 0$) cases of cavity 3 and cavity 4, emission occurs at the triplet energy. In cavity 3, this emission is narrow and well defined about the LP and triplet energy, akin to that observed in cavity 1 and cavity 2. However, cavity 4 shows a broadened emission about the LP and triplet energy, and a significant dip in emission intensity. We propose this to be a signature of

efficient energy transfer to triplet states, as this excited-state energy is stored in the dark triplet (*storage*) states. Cavity 5, the most negatively detuned microcavity, shows emission starting at the triplet state and broadening to the LP energy.

These observations are summarized in Figs. 4(a) and 4(b) where we plot the emission intensity and linewidth (normalized with respect to cavity 1) as a function of ΔE . Using the open quantum system model based on the Jaynes-Cummings Hamiltonian detailed in the Supplemental Material [47], it is possible to fit the measured relative change in the fluorescent emission intensity, from which we learn that the transfer of energy to the storage layer occurs *via* mechanism 2. This fit results in an estimate for the weak triplet-cavity coupling J_T of $\approx 5 \text{ meV}$, as shown in Fig. 4.

B. Time-resolved emission

While the results from steady-state emission spectroscopy allowed us to monitor the effect of cavity-triplet

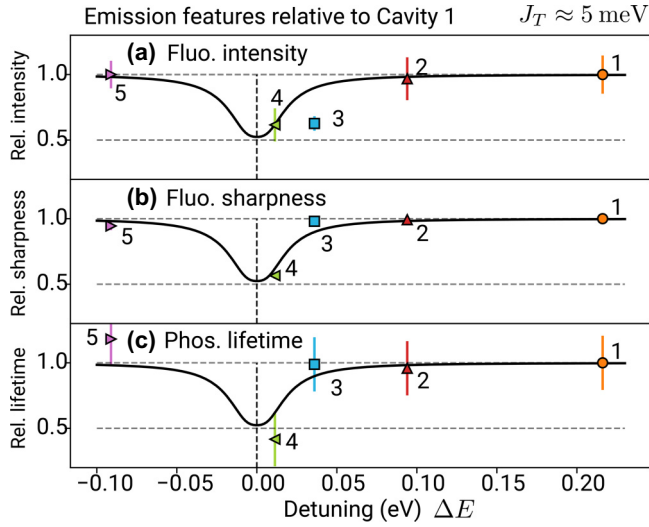


FIG. 4. Triplet-LP resonance signature via fluorescence and phosphorescence emission. Relative change in the fluorescence and phosphorescence emission features, with reference to cavity 1. Fluorescence intensity (a) and sharpness (b), here defined as the inverse of the emission broadness ($1/\text{FWHM}$ of the emission peaks) are expected to decrease around $\Delta E = 0$ as the LP (fluorescent emitter) is depopulated in favor of the triplets. Note that the fluorescent intensity of each device has been normalized to its fluorescent intensity without the cavity, i.e., without the top mirror. Conversely, the decay rate of phosphorescence, proportional to the inverse of the triplet lifetime (c), is expected to increase around $\Delta E = 0$, as the molecular triplets (phosphorescent emitters) mix with the LP. We fit these relative features using a model discussed in the Supplemental Material [47] to obtain a qualitative estimate of the triplet-cavity coupling $J_T \approx 5$ meV.

detuning ΔE on the transfer of energy into the storage layer, time-resolved photoluminescence measurements allow us to monitor the energy storage time of the devices.

We find that fluorescence-dominated emission decreases as $\Delta E \rightarrow 0$ since LP-triplet hybridization reduces emission brightness at short timescales (i.e., < 15 ns). Instead, when looking at *phosphorescence* emission at longer timescales (i.e., > 50 ns), we expect to see an increase in the phosphorescence emission and decay rate as we approach $\Delta E \rightarrow 0$, since the triplets become increasingly mixed with the LP.

This phosphorescence is much lower in intensity compared to fluorescence-dominated emission, persisting over long timescales. In this timescale, we can isolate the time-resolved decay of phosphorescence, which is a proxy for the decay of triplets, and thus, a measure of their population and associated energy storage by the device. In these measurements, the devices were illuminated with pulsed 520-nm laser irradiation at approximately 50 nW. “Short” timescales were acquired at a temporal resolution of 0.05 ns, and “long” timescales were acquired at a temporal resolution of 12.8 ns. Polariton emission is

expected to occur on a picosecond timescale [57], beyond the resolution of our instrumentation. With this in mind, we now consider time-resolved emission for the microcavity devices.

R6G emission lifetime outside the cavity was measured to be 1.48 ± 0.01 ns, compared with a lifetime inside the cavity of 1.10 ± 0.02 ns. Due to inefficient ISC in R6G, the decrease in fluorescence lifetime is assigned to the short lifetime of polaritons: due to strong cavity-R6G coupling, the molecule can radiate light faster.

PdTPP fluorescent emission lifetime outside the cavity was measured to be 1.7 ± 0.1 ns, compared with a lifetime inside the cavity of 1.6 ± 0.1 ns. On the other hand, outside the cavity, the phosphorescent lifetime of PdTPP was measured to be 40.0 ± 0.4 μ s, compared with a lifetime inside the cavity of 57 ± 2 μ s. Figure 4(c) compares the the phosphorescence lifetime for each device, normalized to cavity 1. As $\Delta E \rightarrow 0$, the phosphorescence decay rate γ_{ph} increases, leading to a shorter triplet lifetime as the latter hybridises with the LP. These results are shown in Fig. 4, where the phosphorescence lifetime (γ_{ph}^{-1}) dips for cavity 4, around $\Delta E = 0$, by about 50% with respect to the other devices.

IV. DISCUSSION

Using our Jaynes-Cumming model we deduce that, at resonance ($\Delta E = 0$), the population of molecular triplet states in the storage layer reaches a value of approximately 50%, as shown by the results of Fig. 4, resulting in storage of energy with a self-discharge time of 40.3 ± 0.4 μ s in cavity 4, a clear demonstration of extended energy storage. This self-discharge time is at least 3 orders of magnitude longer than associated with the devices studied by Quach *et al.* [20], which are limited by the radiative fluorescence emission rate of Lumogen-F orange (about 1 ns).

From our results, we can estimate the stored energy density and self-discharge time of the device. The energy density $\rho_E = p_T \cdot E_T \cdot \rho_T$, is proportional to the fraction of excited molecular triplets p_T , their energy E_T and their density in the device $\rho_T \approx 3.01 \times 10^{18}$ cm^{-3} . Assuming that at resonance $p_T \approx 0.5$, the energy density is estimated to be around $\rho_E \approx 2.63 \times 10^{18}$ eV cm^{-3} . The total battery capacity C , achieved when the triplet states are fully populated, is approximately $C = E_T \cdot n_T \approx 1.23 \times 10^{14}$ eV ≈ 5.47 μ Wh, where n_T is the total number of PdTPP molecules in the device. Let us now discuss how much of the stored energy can be converted into useful work. This is done by evaluating the *ergotropy* [42,58–64], which quantifies the maximal amount of work that can be extracted via some process Φ ,

$$\mathcal{E} := \text{Tr} \rho H_0 - \min_{\{\Phi\}} \text{Tr} [\Phi[\rho]^\dagger H_0], \quad (6)$$

where H_0 is the internal Hamiltonian of the system and $\{\Phi\}$ represents the set of accessible operations. The latter can be restricted to unitary operations, which preserve the entropy of the system, or be as general as possible. Here, we calculate the ergotropy of the steady state that is obtained at resonance for mechanism 2, using the simplified three-state model given by the ground state (with energy 0), the lower polariton (with energy E_{LP}) and the triplet (with energy E_T), associated with a Hamiltonian $H_0 = \text{diag}(0, E_{LP}, E_T)$. At resonance, $E_{LP} \approx E_T$, the steady state reads $\rho_\infty \approx (1 - 2p_T, p_T, p_T)$, with $p_T \in [0, 1/2]$. If energy is extracted via unitary operations (reversible and isentropic), the ergotropy is obtained by inverting the population of the ground and triplet states to obtain $\rho_U^* = (p_T, p_T, 1 - 2p_T)$,

$$\mathcal{E}_U = \text{Tr}[\rho_\infty H_0] - \text{Tr}[\rho_U^* H_0], \quad (7)$$

$$= E_T(3p_T - 1). \quad (8)$$

As a result, the ergotropy vanishes for $p_T = 1/3$ (maximally mixed state) and is maximal for $p_T = 1/2$, being $\mathcal{E}_U = E_T/2$. If work can be extracted via any process (e.g., irreversible, nonisentropic), assuming that we cannot operate on the lower polariton, the ergotropy is obtained by preparing the state $\rho_\Phi^* = (1 - p_T, p_T, 0)$,

$$\mathcal{E}_\Phi = \text{Tr}[\rho_\infty H_0] - \text{Tr}[\rho_\Phi^* H_0], \quad (9)$$

$$= E_T p_T. \quad (10)$$

Interestingly, this means that if we give up reversibility, energy can be extracted even from the maximally mixed state, since for $p_T = 1/3$ the ergotropy reads $\mathcal{E}_\Phi = E_T/3$. This analysis tells us that only a portion of the energy stored in the triplets can be extracted to produce work. In this sense, the more energy is locked in auxiliary states, e.g., the lower polaritons, the less work can be extracted from the system.

Further energy-storage improvements are possible with our device architecture. In PdTPP, although ISC is almost perfectly efficient, it occurs on the nanosecond timescale [56], which is comparable to the radiative losses of the cavity and the radiative decay of singlet excitons (ps–ns). This negates mechanism 1 since the necessary resonance conditions do not apply. Nevertheless, it is worth mentioning that ultrafast (picosecond) ISC rates, reported by Alías-Rodríguez *et al.* [65], would lead to more efficient energy transfer to the storage layer. Interestingly, metastable triplet states with 1-s lifetimes, realized by An *et al.* [66], could lead to a self-discharge time 9 orders of magnitude longer than that reported in Ref. [20].

Note that, while we demonstrated the energy-storage concept of Fig. 1 through an all-optical experiment, it is feasible to design and implement other kinds of energy-storage layers, which could, for instance, allow energy

extraction in the form of an electrical current. An experimental demonstration of a possible implementation using two-dimensional materials has been recently reported [67].

V. CONCLUSIONS

In this work, we proposed an approach to improve the energy-storage lifetime of Dicke QBs by several orders of magnitude, by introducing an energy-storage layer based on molecular triplet states. We have shown that there are at least two working regimes for these types of devices, presenting experimental data in support of an optically driven mechanism. To identify these regimes and analyze the emission data, we used an open quantum system model based on an effective Jaynes-Cummings Hamiltonian. A key outlook is to extend this model to genuine many-body systems, to study and optimize the performance of these devices. For the latter, we propose to consider three key energy-storage figures of merit connected to the properties of the devices that we have also considered here: (1) the rate at which triplets are populated, which is associated with the *charging power*, (2) the steady-state triplet population, which represents the *stored energy density* in the layer, and (3) the triplet relaxation timescale, which is linked to the *self-discharge time* of the device.

Finally, we would like to point out the other outstanding challenges for Dicke quantum batteries, beyond the specific organic microcavity platform. Firstly, energy density is a great cross-platform challenge for energy storage in quantum systems. The eV band gap offered by excitonic systems can, in principle, deliver energy densities compatible with optoelectronic devices [5]. However, in practice, random intersite interactions (here given by molecular aggregation at high dye concentration) tend to limit the energy density and charging power of these kinds of QBs.

Another interesting research direction is to experimentally study Dicke QBs in the lossless, coherent (or *unitary*) regime typical of “genuine” quantum technologies based on entanglement. In this context, triplet states can be populated coherently [32], for example, by means of microwave driving, as done in electron spin resonance experiments [68]. This challenging avenue could be explored on “cold” platforms such as neutral atoms [69], trapped ions [70], and superconducting systems [71]. Indeed, there are numerous approaches to investigate, any of which could potentially result in the demonstration of a first fully operational QB.

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DATA AVAILABILITY

All data available from corresponding authors by request and also at the online repository [75].

- [1] D. Larcher and J.-M. Tarascon, Towards greener and more sustainable batteries for electrical energy storage, *Nat. Chem.* **7**, 19 (2015).
- [2] M. Armand and J. M. Tarascon, Building better batteries, *Nature* **451**, 652 (2008).
- [3] Y. Ye, *et al.*, Quadruple the rate capability of high-energy batteries through a porous current collector design, *Nat. Energy* **9**, 643 (2024).
- [4] M. N. Leuenberger and D. Loss, Quantum computing in molecular magnets, *Nature* **410**, 789 (2001).
- [5] F. Campaioli, S. Gherardini, J. Q. Quach, M. Polini, and G. M. Andolina, Colloquium: Quantum batteries, *Rev. Mod. Phys.* **96**, 031001 (2024).
- [6] F. C. Binder, S. Vinjanampathy, K. Modi, and J. Goold, Quantacell: Powerful charging of quantum batteries, *New J. Phys.* **17**, 075015 (2015).
- [7] F. Campaioli, F. A. Pollock, F. C. Binder, L. Céleri, J. Goold, S. Vinjanampathy, and K. Modi, Enhancing the charging power of quantum batteries, *Phys. Rev. Lett.* **118**, 150601 (2017).
- [8] C.-K. Hu, J. Qiu, P. J. P. Souza, J. Yuan, Y. Zhou, L. Zhang, J. Chu, X. Pan, L. Hu, J. Li, Y. Xu, Y. Zhong, S. Liu, F. Yan, D. Tan, R. Bachelard, C. J. Villas-Boas, A. C. Santos, and D. Yu, Optimal charging of a superconducting quantum battery, *Quantum Sci. Technol.* **7**, 045018 (2022).
- [9] G. M. Andolina, M. Keck, A. Mari, V. Giovannetti, and M. Polini, Quantum versus classical many-body batteries, *Phys. Rev. B* **99**, 1 (2019).
- [10] S. Julià-Farré, T. Salamon, A. Riera, M. N. Bera, and M. Lewenstein, Bounds on the capacity and power of quantum batteries, *Phys. Rev. Res.* **2**, 023113 (2020).
- [11] D. Ferraro, M. Campisi, G. M. Andolina, V. Pellegrini, and M. Polini, High-power collective charging of a solid-state quantum battery, *Phys. Rev. Lett.* **120**, 117702 (2018).
- [12] S. Haroche, Nobel lecture: Controlling photons in a box and exploring the quantum to classical boundary, *Rev. Mod. Phys.* **85**, 1083 (2013).
- [13] K. Cong, Q. Zhang, Y. Wang, G. T. Noe, A. Belyanin, and J. Kono, Dicke superradiance in solids, *JOSA B* **33**, C80 (2016).
- [14] L. Fusco, M. Paternostro, and G. De Chiara, Work extraction and energy storage in the Dicke model, *Phys. Rev. E* **94**, 052122 (2016).
- [15] K. Higgins, S. Benjamin, T. Stace, G. Milburn, B. W. Lovett, and E. Gauger, Superabsorption of light via quantum engineering, *Nat. Commun.* **5**, 4705 (2014).
- [16] P. A. Erdman, G. M. Andolina, V. Giovannetti, and F. Noé, Reinforcement learning optimization of the charging of a Dicke quantum battery, *Phys. Rev. Lett.* **133**, 243602 (2024).
- [17] A. Crescente, M. Carrega, M. Sassetti, and D. Ferraro, Ultrafast charging in a two-photon Dicke quantum battery, *Phys. Rev. B* **102**, 1 (2020).
- [18] F.-Q. Dou, Y.-Q. Lu, Y.-J. Wang, and J.-A. Sun, Extended Dicke quantum battery with interatomic interactions and driving field, *Phys. Rev. B* **105**, 115405 (2022).
- [19] G. Gemme, G. M. Andolina, F. M. D. Pellegrino, M. Sassetti, and D. Ferraro, Off-resonant Dicke quantum battery: Charging by virtual photons, *Batteries* **9**, 197 (2023).
- [20] J. Q. Quach, K. E. McGhee, L. Ganzer, D. M. Rouse, B. W. Lovett, E. M. Gauger, J. Keeling, G. Cerullo, D. G. Lidzey, and T. Virgili, Superabsorption in an organic microcavity: Toward a quantum battery, *Sci. Adv.* **8**, eabk3160 (2022).
- [21] X.-W. Chen, V. Sandoghdar, and M. Agio, Coherent interaction of light with a metallic structure coupled to a single quantum emitter: From superabsorption to cloaking, *Phys. Rev. Lett.* **110**, 153605 (2013).
- [22] R. W. Crisp, J. N. Schrauben, M. C. Beard, J. M. Luther, and J. C. Johnson, Coherent exciton delocalization in strongly coupled quantum dot arrays, *Nano Lett.* **13**, 4862 (2013).
- [23] A. A. Svidzinsky, L. Yuan, and M. O. Scully, Quantum amplification by superradiant emission of radiation, *Phys. Rev. X* **3**, 041001 (2013).
- [24] S. Abera Guebrou, C. Symonds, E. Homeyer, J. C. Plenet, Y. N. Gartstein, V. M. Agranovich, and J. Bellessa, Coherent emission from a disordered organic semiconductor induced by strong coupling with surface plasmons, *Phys. Rev. Lett.* **108**, 066401 (2012).
- [25] B. M. Garraway, The Dicke model in quantum optics: Dicke model revisited, *Philos. Trans. R. Soc. A: Math. Phys. Eng. Sci.* **369**, 1137 (2011).
- [26] S. Prasad and R. J. Glauber, Coherent radiation by a spherical medium of resonant atoms, *Phys. Rev. A* **82**, 063805 (2010).
- [27] V. V. Temnov and U. Woggon, Superradiance and subradiance in an inhomogeneously broadened ensemble of two-level systems coupled to a low- q cavity, *Phys. Rev. Lett.* **95**, 243602 (2005).
- [28] S. Prasad and R. J. Glauber, Polarium model: Coherent radiation by a resonant medium, *Phys. Rev. A* **61**, 063814 (2000).
- [29] M. Gross and S. Haroche, Superradiance: An essay on the theory of collective spontaneous emission, *Phys. Rep.* **93**, 301 (1982).
- [30] R. H. Dicke, Coherence in spontaneous radiation processes, *Phys. Rev.* **93**, 99 (1954).
- [31] M. J. Tayebjee, S. N. Sanders, E. Kumarasamy, L. M. Campos, M. Y. Sfeir, and D. R. McCamey, Quintet multiexciton dynamics in singlet fission, *Nat. Phys.* **13**, 182 (2017).
- [32] M. I. Collins, F. Campaioli, M. J. Tayebjee, J. H. Cole, and D. R. McCamey, Quintet formation, exchange fluctuations, and the role of stochastic resonance in singlet fission, *Commun. Phys.* **6**, 64 (2023).
- [33] S. Davidson, A. Fruchtmann, F. A. Pollock, and E. M. Gauger, The dark side of energy transport along excitonic wires: On-site energy barriers facilitate efficient,

- vibrationally mediated transport through optically dark subspaces, *J. Chem. Phys.* **153**, 134701 (2020).
- [34] S. Davidson, F. A. Pollock, and E. Gauger, Eliminating radiative losses in long-range exciton transport, *PRX Quantum* **3**, 020354 (2022).
- [35] J. Liu, D. Segal, and G. Hanna, Loss-free excitonic quantum battery, *J. Phys. Chem. C* **123**, 18303 (2019).
- [36] J. Q. Quach and W. J. Munro, Using dark states to charge and stabilize open quantum batteries, *Phys. Rev. Appl.* **14**, 1 (2020).
- [37] N. J. Hestand and F. C. Spano, Expanded theory of H- and J-molecular aggregates: The effects of vibronic coupling and intermolecular charge transfer, *Chem. Rev.* **118**, 7069 (2018).
- [38] S. R. Yost, E. Hontz, S. Yeganeh, and T. Van Voorhis, Triplet vs singlet energy transfer in organic semiconductors: The tortoise and the hare, *J. Phys. Chem. C* **116**, 17369 (2012).
- [39] Y.-C. Liang, S.-S. Gou, K.-K. Liu, W.-J. Wu, C.-Z. Guo, S.-Y. Lu, J.-H. Zang, X.-Y. Wu, Q. Lou, L. Dong, *et al.*, Ultralong and efficient phosphorescence from silica confined carbon nanodots in aqueous solution, *Nano Today* **34**, 100900 (2020).
- [40] X. Zhong, T. Chervy, L. Zhang, A. Thomas, J. George, C. Genet, J. A. Hutchison, and T. W. Ebbesen, Energy transfer between spatially separated entangled molecules, *Angew. Chem. Int. Ed.* **56**, 9034 (2017).
- [41] In the Dicke model, each donor and acceptor molecule in the ensembles is treated as an individual system.
- [42] D. Farina, G. M. Andolina, A. Mari, M. Polini, and V. Giovannetti, Charger-mediated energy transfer for quantum batteries: An open-system approach, *Phys. Rev. B* **99**, 1 (2019).
- [43] N. Carlon Zambon, *Chirality and nonlinear dynamics in polariton microresonators*, Theses, Université Paris-Saclay, 2020. <https://theses.hal.science/tel-03035028>.
- [44] D. J. Tibben, G. O. Bonin, I. Cho, G. Lakhwani, J. Hutchison, and D. E. Gómez, Molecular energy transfer under the strong light-matter interaction regime, *Chem. Rev.* **123**, 8044 (2023).
- [45] When the exciton-photon couplings are small enough compared to the other energy scales, i.e., $J_D, J_A \ll \omega_C(\theta), \omega_D, \omega_A$, we can apply the rotating wave approximation to eliminate the counter-rotating terms arising from the exciton-cavity couplings.
- [46] This represents the energy gap between ground S_0 and excited S_1 singlet, also known as the *HOMO-LUMO* gap [72].
- [47] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/bhyh-53np> for details on the transition operators, and the constructions and solution of Eq. (2). The Supplemental Material also contains Refs. [44,49–51, 73,74].
- [48] T. W. Ebbesen, Hybrid light-matter states in a molecular and material science perspective, *Acc. Chem. Res.* **49**, 2403 (2016).
- [49] J. P. Zobel, J. J. Nogueira, and L. González, Mechanism of ultrafast intersystem crossing in 2-nitronaphthalene, *Chem. - Eur. J.* **24**, 5379 (2018).
- [50] J. S. Zugazagoitia, C. X. Almora-Díaz, and J. Peon, Ultrafast intersystem crossing in 1-nitronaphthalene. an experimental and computational study, *J. Phys. Chem. A* **112**, 358 (2008).
- [51] T. Okada, I. Karaki, E. Matsuzawa, N. Mataga, Y. Sakata, and S. Misumi, Ultrafast intersystem crossing in some intramolecular heteroexcimers, *J. Phys. Chem.* **85**, 3957 (1981).
- [52] H. Sternlicht, G. Nieman, and G. Robinson, Triplet-triplet annihilation and delayed fluorescence in molecular aggregates, *J. Chem. Phys.* **38**, 1326 (1963).
- [53] P. Atkins and G. Evans, Magnetic field effects on chemiluminescent fluid solutions, *Mol. Phys.* **29**, 921 (1975).
- [54] R. Forecast, F. Campaioli, and J. H. Cole, Magnetic field effects in triplet-triplet annihilation upconversion: Revisiting atkins and evans' theory, *J. Chem. Theory Comput.* **19**, 7816 (2023).
- [55] D. Dempster, T. Morrow, and M. Quinn, The photochemical characteristics of rhodamine 6g-ethanol solutions, *J. Photochem.* **2**, 343 (1973).
- [56] J. E. Rogers, K. A. Nguyen, D. C. Hufnagle, D. G. McLean, W. Su, K. M. Gossett, A. R. Burke, S. A. Vinogradov, R. Pachter, and P. A. Fleitz, Observation and interpretation of annulated porphyrins: Studies on the photophysical properties of meso-tetraphenylmetalporphyrins, *J. Phys. Chem. A* **107**, 11331 (2003).
- [57] S. Wang, T. Chervy, J. George, J. A. Hutchison, C. Genet, and T. W. Ebbesen, Quantum yield of polariton emission from hybrid light-matter states, *J. Phys. Chem. Lett.* **5**, 1433 (2014).
- [58] A. E. Allahverdyan, R. Balian, and T. M. Nieuwenhuizen, Maximal work extraction from finite quantum systems, *Europhys. Lett.* **67**, 565 (2004).
- [59] M. Lostaglio, K. Korzekwa, D. Jennings, and T. Rudolph, Quantum coherence, time-translation symmetry, and thermodynamics, *Phys. Rev. X* **5**, 021001 (2015).
- [60] J. Goold, M. Huber, A. Riera, L. d. Rio, and P. Skrzypczyk, The role of quantum information in thermodynamics—a topical review, *J. Phys. A: Math. Theor.* **49**, 143001 (2016).
- [61] G. Francica, F. C. Binder, G. Guarnieri, M. T. Mitchison, J. Goold, and F. Plastina, Quantum coherence and ergotropy, *Phys. Rev. Lett.* **125**, 180603 (2020).
- [62] B. Çakmak, Ergotropy from coherences in an open quantum system, *Phys. Rev. E* **102**, 042111 (2020).
- [63] T. Biswas, M. Łobejko, P. Mazurek, K. Jałowiecki, and M. Horodecki, Extraction of ergotropy: free energy bound and application to open cycle engines, *Quantum* **6**, 841 (2022).
- [64] R. Castellano, D. Farina, V. Giovannetti, and A. Acin, Extended local ergotropy, *Phys. Rev. Lett.* **133**, 150402 (2024).
- [65] M. Alías-Rodríguez, C. de Graaf, and M. Huix-Rotllant, Ultrafast intersystem crossing in xanthone from wavepacket dynamics, *J. Am. Chem. Soc.* **143**, 21474 (2021).
- [66] Z. An, C. Zheng, Y. Tao, R. Chen, H. Shi, T. Chen, Z. Wang, H. Li, R. Deng, X. Liu, *et al.*, Stabilizing triplet excited states for ultralong organic phosphorescence, *Nat. Mater.* **14**, 685 (2015).
- [67] J. Dutta, N. Yadav, P. Bhatt, K. Kaur, D. E. Gómez, and J. George, Enhanced energy transfer in cavity QED based phototransistors, *J. Phys. Chem. Lett.* **15**, 8211 (2024).
- [68] B. M. Maune, M. G. Borselli, B. Huang, T. D. Ladd, P. W. Deelman, K. S. Holabird, A. A. Kiselev, I.

- Alvarado-Rodriguez, R. S. Ross, A. E. Schmitz, *et al.*, Coherent singlet-triplet oscillations in a silicon-based double quantum dot, *Nature* **481**, 344 (2012).
- [69] C. S. Adams, J. D. Pritchard, and J. P. Shaffer, Rydberg atom quantum technologies, *J. Phys. B: At. Mol. Opt. Phys.* **53**, 012002 (2019).
- [70] C. D. Bruzewicz, J. Chiaverini, R. McConnell, and J. M. Sage, Trapped-ion quantum computing: Progress and challenges, *Appl. Phys. Rev.* **6**, 021314 (2019).
- [71] A. Blais, A. L. Grimsom, S. M. Girvin, and A. Wallraff, Circuit quantum electrodynamics, *Rev. Mod. Phys.* **93**, 025005 (2021).
- [72] S. S. Zade and M. Bendikov, From oligomers to polymer: Convergence in the HOMO-LUMO gaps of conjugated oligomers, *Org. Lett.* **8**, 5243 (2006).
- [73] L. V. Levshin, M. G. Reva, and B. D. Ryzhikov, Effect of intermolecular interactions on the electronic spectra of rhodamine 6G, *J. Appl. Spectrosc.* **26**, 48 (1977).
- [74] P. Bojarski, Concentration quenching and depolarization of rhodamine 6G in the presence of fluorescent dimers in polyvinyl alcohol films, *Chem. Phys. Lett.* **278**, 225 (1997).
- [75] https://github.com/danielgom3z/PRX_Energy_2025.