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# Coherent Light Harvesting through Strong Coupling to Confined Light

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S *Supporting Information*

ABSTRACT: When photoactive molecules interact strongly with confined light modes, new hybrid light−matter states may form: the polaritons. These polaritons are coherent superpositions of excitations of the molecules and of the cavity photon. Recently, polaritons were shown to mediate energy transfer between chromophores at distances beyond the Förster limit. Here we explore the potential of strong coupling for light-harvesting applications by means of atomistic molecular dynamics simulations of mixtures of photoreactive and non-photo-reactive molecules strongly coupled to a single confined light mode. These molecules are spatially separated and present at different concentrations. Our simulations suggest that while the excitation is initially fully delocalized over all molecules and the confined light mode, it very rapidly localizes onto one of the photoreactive molecules, which then undergoes the reaction.
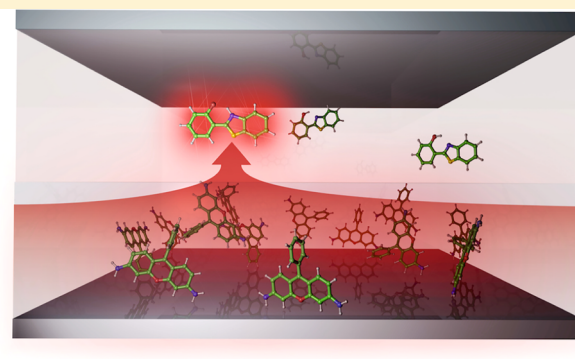
Efficient excitation energy transfer, in which a photon is absorbed in one part of the system but utilized in another, is a key process in both natural and artificial light harvesting.[1,2] Whereas the transfer usually occurs via the well-established Förster or Dexter mechanisms,[3,4] recent experiments[5−8] and theories[9−12] suggest that strong coupling of donor and acceptor molecules with a single confined light mode in an optical cavity can also mediate the transfer, even at distances beyond which the Förster mechanism can operate.[7]

Strong coupling between N molecules and confined light leads to formation of $N + 1$ hybrid light-matter states (so-called polaritons,[13−18] Figure 1b) that are coherent superpositions of excitations in each of the molecules and of the confined light mode[19,20]

$$\psi_K = \sum_{i=1}^{N} \beta_i^K |g_1 g_2 ... e_i ... g_N\rangle |0\rangle + \alpha^K |g_1 g_2 ... g_i ... g_N\rangle |1\rangle \quad (1)$$

Here $|g_i\rangle$ and $|e_i\rangle$ are the ground and excited states of molecule i, while $|1\rangle$ or $|0\rangle$ indicates whether there is a photon in the cavity. The β_i^K and a^K are expansion coefficients, and the index K labels the $N + 1$ eigenstates of the system. When the excitation energy of the molecules ($\hbar\omega_i$) is resonant with the frequency of the confined light mode ($\hbar\omega_c$), the energy gap ($\hbar\Omega^{\text{Rabi}}$) between the lowest ($K = 1$, i.e., the lower polariton) and highest ($K = N + 1$, i.e., the upper polariton) hybrid state is proportional to the square root of the number of molecules (N) that are strongly interacting with the confined light mode

$$\hbar\Omega^{\text{Rabi}} = 2|\vec{\mu}_m| \sqrt{N\hbar\omega_c/\epsilon_0 V_c} \quad (2)$$

where $\vec{\mu}_m$ is the transition dipole moment of the molecules, ϵ_0 is the vacuum permittivity, and V_c is the volume, in which the photon with (angular) frequency ω_c is confined.

Because the lower ($K = 1$) and upper ($K = N + 1$) polaritons have much higher cross sections for light absorption than the other $N - 1$ states, the absorption spectrum of the cavity−molecule system has two peaks instead of one, located below and above the absorption maxima of the cavity and the molecules (Figure 1c). In the lower and upper polaritons, the excitation is coherently shared between all molecules and the confined light mode, whereas in the other $N - 1$ states, the excitation is more localized on subsets of the molecules.

Despite the delocalized character of the excitation into the lower polariton, recent simulations have shown that polaritons follow Kasha's rule and relax into the lowest energy state available to the cavity−molecule system.[21,22] This observation suggests that if there are molecules that can undergo a photochemical reaction to energy levels below the lower polariton, then the coherently shared excitation can collapse and localize the excitation energy onto one of those molecules. Thus polaritonic light harvesting might be achieved if a large number of nonreactive chromophores are combined with a few photoreactive molecules within the volume of a confined light mode that is resonant with both types of molecules. In this situation, all molecules contribute to photon absorption,
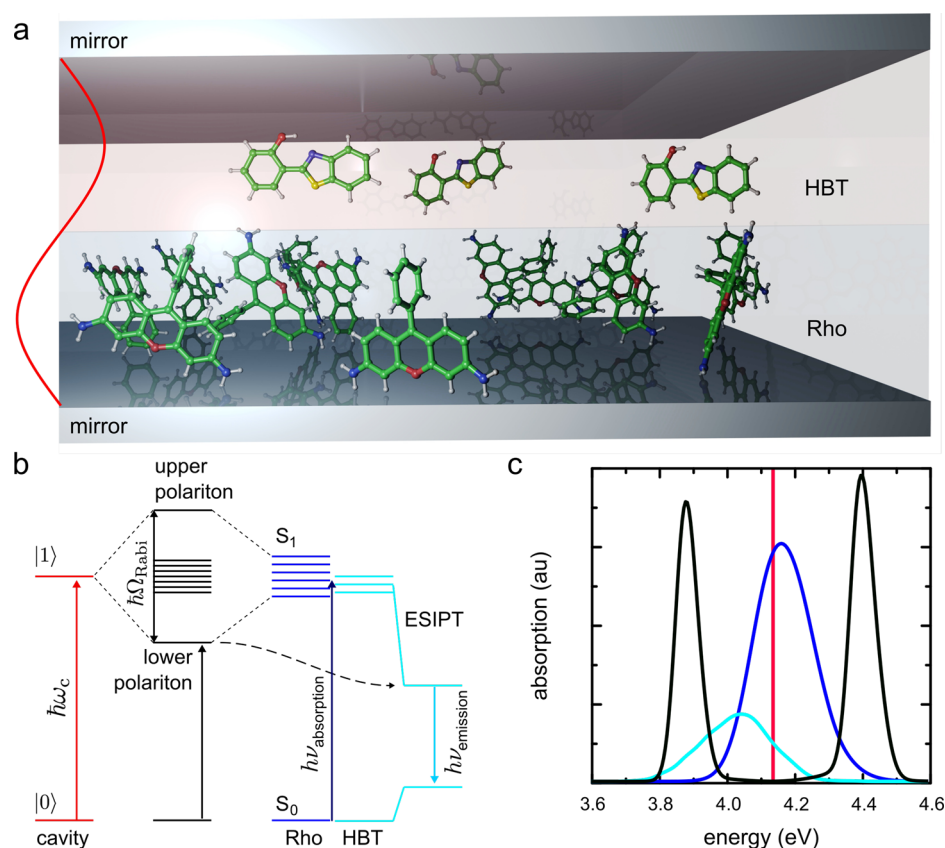
Figure 1. (a) Schematic depiction of the cavity−molecule system (not to scale). Inside the cavity there are two spatially separated layers of chromophores: rhodamine (Rho, blue) and hydroxyphenyl-benzothiazole (HBT, cyan). Because the second mode of the cavity (ω_c, red) is resonant with the excitations of both chromophores, hybrid light-matter polaritons are formed (b). The dashed arrow in panel b indicates that HBT could potentially undergo ultrafast intramolecular proton transfer (ESIPT) to a configuration with an energy below the lower polariton. Because of the red shift associated with this reaction, the HBT molecule is no longer in resonance with the cavity and can localize the excitation. (c) Polariton absorption spectrum (black) with 1000 Rho (blue) and 10 HBT molecules (cyan) strongly coupled to the confined light mode of the cavity (red).

whereas only one molecule eventually uses that energy for the reaction (Figure 1b).

Light can be efficiently confined between the mirrors of a Fabry-Pérot optical cavity[23] or on the surface of metallic nanoparticles supporting a localized surface plasmon resonance (LSPR).[24,25] Because in our simulations the details of the actual structure for confining light are irrelevant,[21] our results will be valid for both types of light confinement. However, because of the high reflectivity of the mirrors, optical cavities are not very suited for light-harvesting applications. Therefore, practical realizations would more likely have to rely on open nanoparticle-based structures instead.

To test the idea, we constructed atomistic models with both reactive and nonreactive chromophores coupled to a single confined light mode that is resonant with their optical transitions. We assume that our cavity has an infinite quality (Q) factor. Thus a photon can be trapped between the mirrors forever and the cavity excitation never decays. To account for the effect of the light−matter coupling on the dynamics of the N molecules, we followed Galego et al.[26] to extend the traditional Jaynes−Cummings model[19,20] for molecules inside cavities.[21] To obtain the N + 1 polaritonic states (eq 1), the electronic ground and excited states of each molecule were calculated at the QM/MM level[27] as well as their transition dipole moments. As explained in the Supporting Information (SI) and in ref 19, we use these energies and dipole moments to construct the light-matter Hamiltonian matrix that we

diagonalize at every time step of the simulation to obtain the polaritonic potential energy surfaces and eigenstates. The dynamics of all molecules are propagated simultaneously on a single polaritonic potential energy surface, whereas transitions between the surfaces are modeled with a surface-hopping algorithm.[28]

The very fast decay rate of cavity photons restricts the choice of photoreactive molecules to those with reaction rates within the polariton lifetime. Here we have selected 2-(2′-hydroxyphenyl) benzothiazole (HBT), which undergoes ultra-fast (∼30 fs) excited-state intramolecular proton transfer (ESIPT) upon photoexcitation (Figure 2).[29] This reaction is readily observed as a very large red shift in the emission from ultraviolet (UV, 340 nm) to green (525 nm). In line with results from previous simulation studies[30] and experiments,[29]
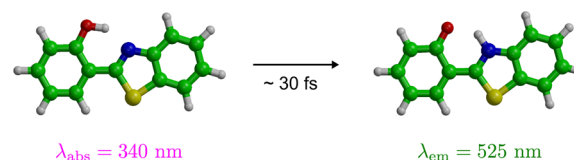

Figure 2. Upon excitation with ultraviolet (UV) light at 340 nm, HBT undergoes ultrafast intramolecular proton transfer, which causes the emission to red-shift to 525 nm. Carbon atoms are green, oxygen is red, nitrogen is blue, sulfur is yellow and hydrogens are white.

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HBT undergoes proton transfer within tens of femtoseconds after photon absorption in QM/MM simulations (SI).

For the nonreactive molecules, we used the rhodamine model introduced in previous work.[21] In this model, the rhodamine has an absorption maximum at 4.15 eV, which is close to the excitation maximum of HBT (4.05 eV) in our simulations (Figure 1c). The simulated cavities contained up to 1000 rhodamines and 10 HBT molecules in spatially separate layers, as in previous experiments.[7] Both rhodamine and HBT layers were simultaneously coupled to the second confined light mode of the cavity with energy $\hbar\omega_c$ = 4.13 eV (Figure 1a).

After ground-state equilibration, the combined molecule–cavity system is resonantly excited into the optically active lower polariton at 3.9 eV (Figure 1c). Initially, the excitation is fully delocalized over all molecules and the confined light mode of the cavity (Figure 3a). Because there is much more
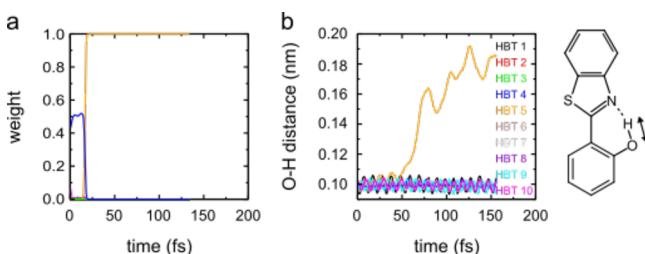

Figure 3. (a) Time evolution of the lowest energy polaritonic state during an MD simulation of 10 HBT and 1000 Rho molecules in an optical cavity resonant with the molecular excitations. Plotted in panel a are the weights of the excitations on each molecule ($|\beta_i^{LP}|^2$ in all colors; $|\beta_{1005}^{LP}|^2$, with the fifth HBT molecule excited, in orange) and cavity photon ($|\alpha^{LP}|^2$, blue, eq 1). (b) Distance between the donor oxygen (O) and proton (H). About 30 fs after localization of the excitation onto the fifth HBT molecule (orange), proton transfer to the nitrogen (N) occurs, as evidenced by the increase in the O−H distance. In the remaining nine HBT molecules, the O−H distance fluctuates around the ground-state equilibrium bond length.

rhodamine than HBT and because rhodamine also has a larger transition dipole moment, the excitation mostly resides in the rhodamine layer (175:1). However, within 20 fs, the excitation localizes onto a single HBT molecule. After the collapse of the initially coherent excitation onto this HBT molecule, its hydroxyl proton transfers rapidly from the oxygen to the nitrogen atom, as shown in Figure 3b.

We repeated the simulations with various combinations of the molecules, keeping the HBT/rhodamine ratio identical. Also, in these simulations, the excitation is initially delocalized over all molecules but rapidly localizes onto one of the HBT molecules. These results, presented in the SI and summarized in Table 1, suggest that the variations have little effect on the efficiency of the excitation energy-transfer process under strong coupling. Because in most simulations the localization of the coherent excitation precedes proton transfer by several tens of femtoseconds, the photonic structures used for confining the light do not require long photon lifetimes or high Q factors. Therefore, if the energy levels, mode volumes and relaxation rates of the photonic structure are sufficient to reach the strong coupling limit for both molecules, then it is not relevant whether these are achieved with Fabry-Pérot cavities or with plasmonic surfaces, arrays or nanoparticles.

In summary, our atomistic simulations suggest that strong coupling can be utilized to achieve ultrafast and directional

Table 1. Number of Trajectories, Time of Excitation Localization, Time of Proton Transfer, and Rabi Splitting with Various Numbers of HBT and Rhodamine Molecules and Vacuum Field Strengths

HBT/Rho	trajectories	vacuum field (au)[a]	collapse (fs)	ESIPT (fs)[b]	Rabi split (eV)[c]
10/1000	1	0.00008	19[d]	65[d]	0.53
5/500	2	0.00010	26 ± 8	83 ± 25	0.47
1/100	10	0.00020	53 ± 13	145 ± 22	0.42

[a]Vacuum field is defined as $\sqrt{\hbar\omega_c/\epsilon_0 V_c}$ (eq 2) in atomic units of energy and dipole moment and was chosen to yield a Rabi splitting of ∼0.5 eV in all simulations. [b]Time at which the O−H distance exceeds 0.125 nm. [c]Rabi splitting at the start of the simulation. [d]No error is estimated when there is only one trajectory.

transfer of excitation energy into a single photoreactive molecule. A layer of concentrated chromophores with large transition dipole moments inside a cavity or near a plasmonic nanostructure provides high oscillator strength, while a layer of low-concentration photoreactive molecules collects the energy necessary for their photochemical reactions. Although in this work, the acceptor of the excitation energy undergoes proton transfer, photovoltaic applications would aim for electron transfer instead. Via nanofabrication, such photo-oxidation reactions can be made to occur inside an optimal chemical environment, shielded from the other photoactive molecules, thereby preventing radiation damage or recombination.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jp-clett.8b02032.

Full methodological description of the cavity QM/MM simulations, QM/MM models and their validation, and tables and figures with data from all trajectories (PDF)

QuickTime animation of excited-state intramolecular proton transfer in an isolated HBT molecule (MOV)

QuickTime animation of excited-state intramolecular proton transfer in an HBT molecule that is inside a cavity with four other HBT and 500 Rho molecules (MOV)

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Notes
The authors declare no competing financial interest.

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