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LONG-DISTANCE OPERATOR FOR ENERGY TRANSFER

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Nonradiative energy transfer is a ubiquitous phenomenon in nature. Photosynthesis begins with light harvesting, where pigment-protein complexes transform sunlight into excitations, usually called excitons, within the molecules. Excitons are formed by an excited electron and the positively charged hole that is left in the ground state. In photosynthesis, the energy of this exciton is finally transferred to the reaction center, where a charge separation process provides chemical energy for plants, algae, and bacteria. Human-made organic photovoltaic cells try to mimic this natural process, and it is the transport of the excitons after light absorption that determines the efficiency of the cell. In organic materials, energy transfer is governed by short-range dipole-dipole interactions through the process of Förster resonance energy transfer (FRET), whose spatial range is limited to distances less than 10 nm. Recent work by Zhong et al. (1) shows how this range can be extended to distances larger than 100 nm by taking advantage of a quantum electrodynamics (QED) phenomenon called strong coupling.

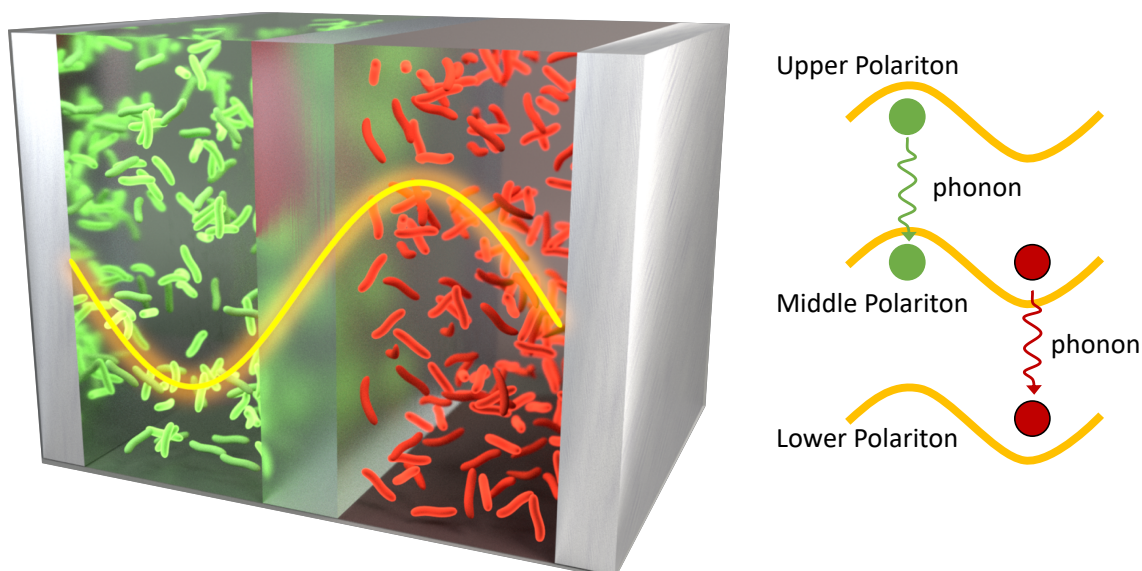
The short range of FRET is a consequence of the small interaction between visible light (a photon) and matter (an exciton) in vacuum. However, this coupling can be increased (or decreased) if the photonic environment of the exciton is modified. For example, when a molecule is located inside a cavity able to confine electromagnetic (EM) fields, the light-matter interaction is enhanced. In such systems, two different regimes of light-matter coupling can be distinguished. In the weak-coupling limit, the absorption and emission rates of a photon by the molecule are modified by the presence of a “dressed” vacuum. By using different nanophotonic structures, this weak coupling regime has been exploited to expand the range of FRET between molecules (2, 3). In the strong-coupling regime, the interaction between light and matter is so strong that the photon and exciton components mix to create new hybrid light-matter states called polaritons.

Organic molecules present a favorable case to reach strong coupling (4, 5), as their excitons possess large dipole moments and they can be tightly packed, thereby increasing the coupling strength for collective light-matter interaction. A new area of interdisciplinary research devoted to taking advantage of this QED phenomenon of strong coupling to enhance the capabilities of organic materials has emerged. Some experiments have already shown modifications of chemical reaction rates (6), and there have been proposals to completely suppress photochemical reactions (7) by means of strong coupling. One of the biggest assets of QED strong coupling is that polaritons, in contrast to excitons that are localized around a given molecule, extend over the entire structure. In a naïve way, we can view polaritons as “supermolecules” involving all the molecules as well as the confined EM field. This effect has important implications from a materials science perspective. An increase in the electrical conductance of an organic material under strong coupling with surface plasmon EM modes supported by a thick

metal film was reported recently (8). Along this line, it has been predicted that exciton transport can also be dramatically enhanced by the same QED effect (9, 10). Furthermore, by properly designing the electric field profile of the confined EM mode, exciton harvesting and funneling can be achieved (11); excitons could then be guided from a collection area to a desired long-distance location.

The delocalized character of polaritons has already been exploited for FRET between different molecular species. Polariton-mediated efficient and ultrafast FRET between the excitons of donor and acceptor molecules was reported (12, 13). In these experiments, the two types of dyes were located within a microcavity but were spatially intermixed. By contrast, Zhong et al. (1) physically separated the two ensembles of molecular dyes. They placed the J-aggregates of two cyanine dyes (one acting as donors, the other as acceptors) within a Fabry-Perot cavity formed by two silver mirrors and a polymer spacer between the two molecular layers (see the figure). The donor and acceptor layers are located at the antinodes of the second EM mode supported by the cavity in order to favor the emergence of strong coupling. This leads to three polariton modes where the excitonic component is either dominated by donors (upper polariton) or acceptors (lower polariton), or formed by a mixture between the two (middle polariton). When donor molecules are excited, energy is first stored in the upper polariton. The exciton energy is then released through local exciton-vibration interactions in the donor molecules to the middle polariton and from there, by the same mechanism in the acceptor molecules, to the lower polariton. In this way, polaritons act as long-distance operators between the two ensembles of molecular dyes. An energy transfer efficiency of 37% is reported for distances between molecular layers larger than 100 nm, although this mechanism would allow FRET over much longer distances because it does not rely on dipole-dipole interactions but only on the spatial extent of the polaritons.

From a quantum perspective, polaritons are a superposition of product states (a ground-state molecule and a photon in the cavity, plus an excited-state molecule with an empty cavity), and are thus closely related to entangled states as studied in quantum information theory. This suggests that local exciton-vibration interactions can have nonlocal effects. From this viewpoint, the long-range energy transfer observed by Zhong et al. can be understood as the result of a process in which polaritons provide entanglement between acceptor-donor states and automatically transform local interactions into nonlocal ones. Apart from the immediate prospect of further extending the range of polariton-mediated FRET for practical purposes, it will be interesting to explore whether other concepts of entanglement as a resource can be applied in the case of organic polaritons.



Cavity-mediated energy transfer: A cavity formed by two silver mirrors supports an electromagnetic mode (yellow line) whose two intensity maxima coincide with the locations of spatially separated donor (green) and acceptor (red) molecules. Taking advantage of the collective nature of polaritons, excitons can jump directly from donor to acceptor molecules.

Bibliography

- (1) X. Zhong, Th. 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).
- (2) P. Andrew and W. L. Barnes, Energy Transfer Across a Metal Film Mediated by Surface Plasmon Polaritons, *Science* 306, 1002 (2004).
- (3) S. Götzinger, L. de S. Menezes, A. Mazzei, S. Kühn, V. Sandoghdar, and O. Benson, Controlled Photon Transfer between Two Individual Nanoemitters via Shared High-Q Modes of a Microsphere Resonator, *Nanolett.* 6, 151 (2006).
- (4) I. Pockrand, A. Brillante, and D. Möbius, Exciton–surface plasmon coupling: An experimental investigation, *J. Chem. Phys.* 77, 6289 (1982); D. G. Lidzey, D. Bradley, M. S. Skolnick, and T. Virgili, Strong exciton–photon coupling in an organic semiconductor microcavity, *Nature* 395, 53–55 (1998).
- (5) J. A. Hutchison, T. Schwartz, C. Genet, E. Devaux, and T. W. Ebbesen, Modifying Chemical Landscapes by Coupling to Vacuum Fields, *Angew. Chemie* 124, 1624 (2012).
- (6) J. Galego, F. J. Garcia-Vidal, and J. Feist, Suppressing photochemical reactions with quantized light fields, *Nature Comm.* 7, 13841 (2016).
- (7) E. Orgiu, J. George, J. A. Hutchison, E. Devaux, J. F. Daven, B. Doudin, F. Stellacci, C. Genet, J. Schachenmayer, C. Genes, G. Pupillo, P. Samori, and T. W. Ebbesen, *Nature Mat.* 14, 1123 (2015).
- (8) J. Feist and F. J. Garcia-Vidal, Extraordinary exciton conductance induced by strong coupling, *Phys. Rev. Lett.* 114, 196402 (2015).
- (9) J. Schachenmayer, C. Genes, E. Tignone, and G. Pupillo, Cavity-Enhanced Transport of Excitons, *Phys. Rev. Lett.* 114, 196403 (2015).

- (10) C. Gonzalez-Ballester, J. Feist, E. Moreno, and F. J. Garcia-Vidal, Harvesting excitons through plasmonic strong coupling, *Phys. Rev. B* 92, 121402(R) (2015).
- (11) D. M. Coles, N. Somaschi, P. Michetti, C. Clark, P. G. Lagoudakis, P. G. Savvidis, and D. G. Lidzey, Polariton-mediated energy transfer between organic dyes in a strongly coupled optical microcavity, *Nature Mat.* 13, 712 (2014).
- (12) X. Zhong, Th. Chervy, S. Wang, J. George, A. Thomas, J. A. Hutchison, E. Devaux, C. Genet, and T. W. Ebbesen, Non-Radiative Energy Transfer Mediated by Hybrid Light-Matter States, *Angew. Chem. Int. Ed.* 55, 6202 (2016).