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Plasmon mediated energy transfer between two systems out of equilibrium

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Abstract

2
3
4 The fabrication of nanostructured samples assembling organic, inorganic emitters
5 and plasmons has been widely explored in the last decades in the context of energy har-
6 vesting applications or for the design of optoelectronic devices. However, understanding
7 the interaction between each component in such a complex scenario is a challenge. Here
8 we report on the energy transfer between ensembles of inorganic quantum dots and or-
9 ganic J-aggregates mediated by surface plasmon polaritons. The two emitters' species

[#] These authors contributed equally to this work.

10 are spatially separated on the surface of a continuous silver film in an optically struc-
11 tured sample in order to measure the impact of their relative separation on the energy
12 transfer. We introduce a theoretical model of the photoluminescence of the system to
13 quantify the energy transfer between the two species through the chemical potential of
14 photons.

15 **Keywords**

16 Surface plasmons - energy transfer - strong coupling - Local Kirchhoff's law - organic-
17 inorganic emitters - photoluminescence - Brendel Borman model

18 **Introduction**

19 Coupling organic and inorganic materials has brought a lot of attention in the last decades
20 for various purposes such as energy harvesting in solar cells,¹ hot electron transfer,² pho-
21 tocatalysis³ and optoelectronic devices.⁴ Hybrid devices of these materials are appealing to
22 overcome their limitations when used separately.⁵ On one hand, organic materials, such as
23 J-aggregated molecules, show a large absorption cross section, high oscillator strength and
24 thus strong light-matter interaction. On the other hand, inorganic materials, such as quan-
25 tum dots (QDs), are photostable, have enhanced optical non-linearity and high electrical
26 conductivity. In the case of quantum dots, the emission spectrum is rather narrow band and
27 the maximum emission wavelength is directly related to the QDs' diameter, which makes
28 them very versatile fluorescent nano-objects. Enabling energy transfer between organic and
29 inorganic materials merges together the best of both worlds, as it has been shown in the
30 recent literature.⁶ One approach to increase the efficiency as well as the range of the energy
31 transfer is to shape a favouring electromagnetic environment of the materials e.g. embedding
32 the materials in a microcavity,⁷⁻¹⁰ creating electromagnetic hotspots with metallic nanopar-
33 ticles^{11,12} or surface plasmon polaritons.^{13,14} However, understanding the role played by the

34 different components is a hard task, due to the formation of hybrid modes, and to the spa-
35 tial and spectral overlap between emitters' ensembles and plasmonic modes. Note also that
36 ensembles of emitters cannot be considered as a mere superposition of independent single
37 emitters, and an appropriate theoretical model has to be used.¹⁵

38 In this paper, we explore a multilayer system in which organic (J-aggregated TDBC) and
39 inorganic (QDs) ensembles of fluorescent emitters interact with a surface plasmon polariton
40 (SPP) propagating over a distance of a few microns. The interaction of SPPs' confined
41 field and large oscillator strength of organic molecules results in the formation of hybrid
42 extended modes and the observation of light-matter strong coupling.^{16,17} We take advantage
43 of the micrometric propagation length of the SPP to spatially separate regions in which
44 the inorganic material interacts with the SPP to regions in which it interacts with strongly
45 coupled hybrid modes. This modulates the energy transfer between the inorganic material
46 and the organic material via surface polaritons modes. Numerical simulations based on
47 the local Kirchhoff's law to model light emission by an ensemble of thermalized emitters¹⁸
48 enable to quantify the energy transfer between the two ensembles of fluorescent emitters
49 through SPP coupling. More precisely, we introduce a chemical potential to characterize
50 quantitatively the energy transfer to the molecules. Simulations are in very good agreement
51 with the experiments.

52 **Description of the sample and the experimental method**

53 The sample under study is sketched in Fig.1a and its fabrication is detailed in the Methods
54 section. It consists of a $t_{\text{Jagg}} = 17$ nm thick layer of J-aggregated TDBC deposited on
55 top of a $t_{\text{Ag}} = 50$ nm thick silver film laying on a glass coverslip. Then, we deposited
56 on top a $t_{\text{QD}} = 15$ nm thick layer of QDs embedded in a polymer matrix of PMMA. The
57 thicknesses above are measured with an Atomic Force Microscope (AFM). We measure the
58 photoluminescence (PL) of the system in the reciprocal space to visualize the available

59 electromagnetic modes through their dispersion relation.

60 The spectral properties of each ensemble of emitters on glass are presented in Fig.1b.
61 The absorption and PL spectra of the J-aggregates are narrow and their maxima are cen-
62 tered at 585 nm and 595 nm respectively. The QDs absorption spectrum is characterized by
63 a large band increasing towards short wavelengths and an exciton resonance at 526 nm while
64 the QDs PL spectrum has a maximum at $\lambda_{\text{QDs}} = 576$ nm and partially overlaps the absorp-
65 tion spectrum of the J-aggregates making our system suitable for observing energy transfer
66 effects. The presence of the silver layer modifies the spectra with respect to the spectra ob-
67 tained on glass. The experimental reflectance of the complete sample, which is reported in
68 Fig. 1c, shows the presence of the so-called lower polariton (LP) and upper polariton (UP)
69 branches that anticross indicating a strongly coupled system.¹⁹ The anticrossing occurs at
70 the resonance between the J-aggregates exciton (at 2.1 eV) and the SPPs propagating at the
71 interface between the silver and the two dielectric layers, with a corresponding Rabi splitting
72 of 153 meV.

73 In such a multilayer sample, energy transfer between the different layers influences the
74 optical properties of the entire system. Understanding the role played by each layer in the
75 definition of the optical properties and in the energy transfer is a complex task. To disentangle
76 the contribution of the different components, we study a sample where the J-aggregated
77 TDBC is prepared in a non-absorbing state. By comparing the optical properties obtained
78 when the excitation laser illuminates a region in which J-aggregates are photobleached with
79 the optical properties obtained in a region in which they are not, energy transfer can be
80 studied. Moreover, we study samples shown in Fig. 2a. consisting in a disk with photo-
81 bleached TDBC molecules surrounded by the system with non photobleached molecules. We
82 excite the QDs at the center of the disk so that the energy transfer between the QDs and
83 the TDBC molecules can be studied as a function of the radius of the disk. This study can
84 assess the possibility of surface plasmon mediated energy transfer.

85 Locally photobleached J-aggregates areas are obtained by shining a high intensity UV

86 irradiation laser writer ($\lambda = 365 \text{ nm}$)²⁰ on the J-aggregated TDBC layer before the deposition
 87 of the QDs. Photobleached J-aggregates have been shown to have the same refractive index
 88 as the active dye film, except in the spectral region around 2.1 eV where the absorption peak
 89 is removed.¹⁷ An optical microscopy image of the sample after irradiation is shown in Fig.
 90 2a. The circular photobleached areas (CPAs) have a diameter ranging from 1 to 10 μm by
 91 steps of 1 μm and two larger diameters of 20 and 40 μm . As 40 μm is significantly larger than
 92 the SPP propagation length (set to 2.21 μm at 570 nm, defined as $1/(2k'')$, see Methods),
 93 the central area of the later sample can be taken as a reference medium whose properties
 94 are not influenced by the J-aggregated TDBC.

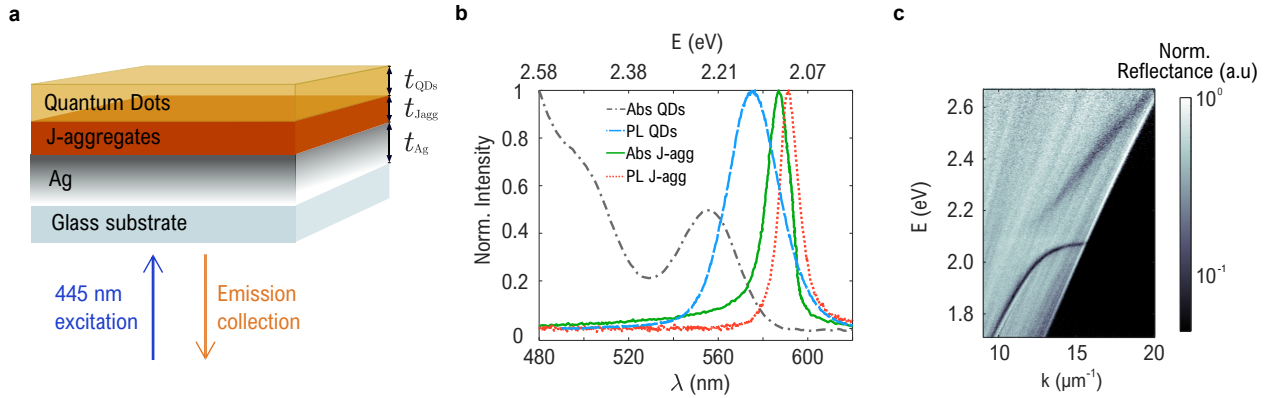


Figure 1: a) Sketch of the multilayered sample consisting of a silver film of $t_{\text{Ag}} = 50 \text{ nm}$, a J-aggregates layer of $t_{\text{Jagg}} = 17 \text{ nm}$, and a QDs/PMMA layer of $t_{\text{QDs}} = 15 \text{ nm}$. Such values are measured with an Atomic Force Microscope (AFM) on the sample. We excite the sample with a 445 nm laser excitation through the silver film and we collect the resulting fluorescence from the same side. The excitation wavelength is chosen in a spectral region in which the absorption cross-section of the QDs is high while the one of the J-aggregated TDBC is low. b) Absorption and PL spectra of thin films of QDs and J-aggregated TDBC deposited on glass. c) Reflectometry measurement (in logarithmic scale) of the sample showing the strongly coupled polaritons with a Rabi splitting of 153 meV.

95 We investigate the system through the measurements of PL spectra resolved in the sample
 96 in-plane wavevector k . For this purpose, the sample sits on an inverted microscope and
 97 the patterned multilayer is excited by a pulsed laser beam ($\lambda = 445 \text{ nm}$) focused on it
 98 through the glass coverslip. The laser is focused on a diffraction limited spot through a
 99 high numerical aperture oil immersion objective (NA=1.5) and the radiation leaking from

100 the excited propagating modes is collected through the same objective. The excitation
 101 wavelength is chosen in a spectral region in which the absorption cross-section of the QDs is
 102 high while the one of the J-aggregated TDBC is low. We collect the TM-polarized emission
 103 over a field of view of $\sim 20 \mu\text{m}$, and image the back focal plane of the microscope objective
 104 onto the slit of a spectrometer coupled to an EMCCD. This image is dispersed by the
 105 spectrometer's diffraction grating to get the spectrum as a function of the wave-vector. The
 106 diffraction limited laser spot enables to locally excite the center of each CPA and to study
 107 the modification of the energy transfer between the QDs and the J-aggregated TDBC when
 108 the CPA radius increases. Figure 2b shows the situation when the center of a CPA is excited.
 109 In the limiting cases with $\Phi_{\text{CPA}} = 40 \mu\text{m}$ and $\Phi_{\text{CPA}} = 0 \mu\text{m}$, the electromagnetic modes are
 110 either SPPs or strongly coupled polaritons respectively.

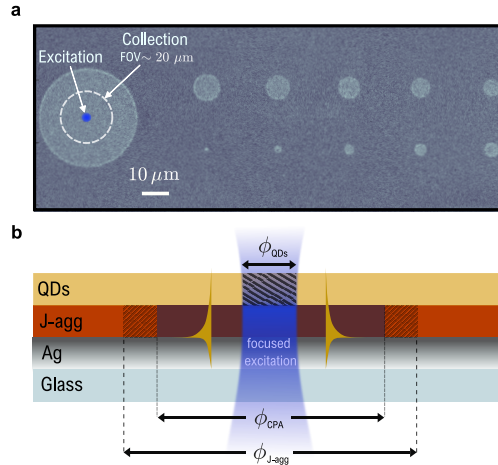


Figure 2: a) Dark-field microscopy image of a lithographed zone of the J-aggregates film deposited on silver. The design of the pattern contains circular photobleached areas (CPAs) with diameters ranging from 1 to $40 \mu\text{m}$. The smallest separation distance between adjacent bleached regions is $20 \mu\text{m}$ to isolate them from each other. The pattern was repeated tens of times within the sample to test the repeatability of the experimental results. In the $40 \mu\text{m}$ CPA, we represented the laser excitation and the detection field of view. b) Sketch of a CPA being illuminated at its center by the focused laser excitation. Following laser excitation, QDs decay by exciting modes propagating in the sample plane. The hatched areas correspond to the volume of excited emitters in which we set a non-zero chemical potential for simulations.

111 Results and Discussion

112 Experimental results are reported on Fig. 3a-f. Let us first consider the case in which we
 113 excite an unbleached homogeneous region containing active J-aggregates topped with the
 114 layer of QDs. The corresponding PL emission spectra as a function of the wavevector is
 115 shown in the $E(k)$ map of Fig. 3a. In such region, the electromagnetic environment is
 116 shaped by the strong light-matter coupling between the J-aggregates and the SPPs, with a
 117 shift to higher wavevectors due to the layer of QDs/PMMA. The anticrossing between the
 118 LP and UP is clearly visible. Interestingly, light is emitted through the UP although it is
 119 not observable in PL measurements when only a J-aggregates layer is present as the active
 120 material on the top of a silver film.^{19,21} In the case of the sample studied in this paper, since
 121 the QDs' energy spectrum overlaps the UP mode, QDs couple to it. The upper polariton
 122 then leaks into a photon. This emitter-photon interaction mediated by the polariton was
 123 first described by Hopfield.²² The LP is also observed. In this case, two mechanisms are
 124 possible: direct emission by the QDs mediated by the LP or energy transfer from the QDs
 125 to the TDBC molecules which then emit through the LP. In what follows, we will introduce
 126 a theoretical model to analyse the data and identify the mechanism at play.

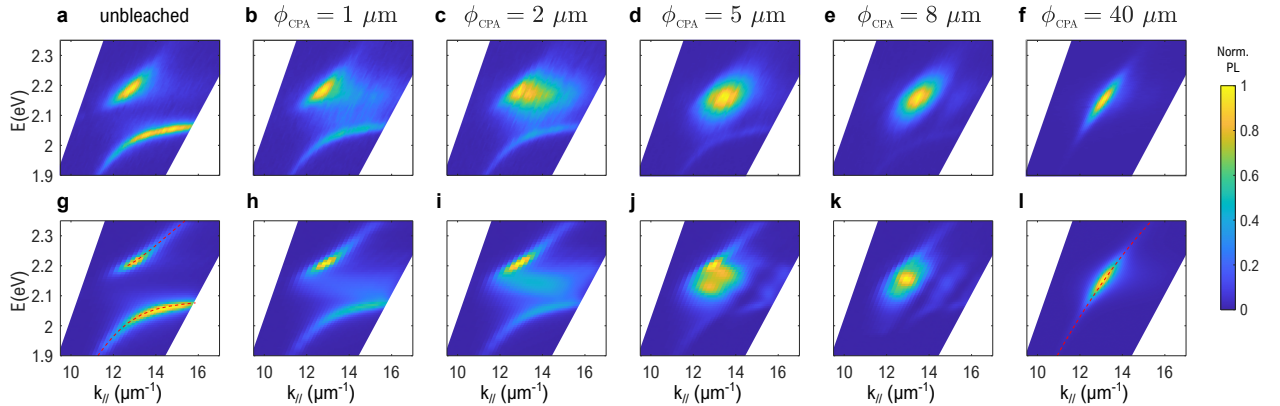


Figure 3: a)-f) Experimental and g)-l) simulated photoluminescence $E(k)$ maps for different regions in the sample. In a) and g) the laser is focused in a region where there is no lithography, i.e the J-aggregates are active. For the other subfigures, the diameter of the CPA is indicated on top of each pair of experimental and simulated results. The experiments are performed with the laser focused at the center of the CPA. The dispersion relations of the polaritons and SPPs are added in red dotted lines in g) and l) respectively.

127 For $\Phi_{\text{CPA}} = 40 \mu\text{m}$, the measured PL spectrum versus k is shown in Fig. 3f. The pattern
128 in the plane (k_{\parallel}, E) indicates an emission mediated by the plasmon propagating in the
129 system with photobleached molecules. In other words, the measurement shows no influence
130 of the TDBC molecules indicating that there is no energy transfer between the QDs and the
131 molecules located $20 \mu\text{m}$ apart. Given that the decay length of the SPP intensity is $2.21 \mu\text{m}$
132 at 570 nm , this behaviour is consistent with a QD-molecule interaction mediated by SPP.

133 We now turn to the intermediate cases with a CPA diameter varying between 1 and $8 \mu\text{m}$
134 (Fig. 3b-e). As sketched in Fig. 2b, the Gaussian laser beam excites the QDs at the center
135 of the disk with the photobleached J-aggregates. The QDs subsequently relax through the
136 available propagating modes. Assuming that the interaction between the QDs and TDBC
137 molecules is mediated by surface plasmon, the distance between the excitation spot and the
138 active J-aggregates is thus a leading feature of the system, as it rules the interaction between
139 the QDs and the strongly coupled modes. In Figures 3b-e, light is unexpectedly detected for
140 values of energy and k vectors at which light emission is not due to SPP, UP or LP. This is
141 evident when comparing these data with the results obtained in the situation without CPA
142 (Fig. 3a, f). A modification of the intensity distribution depending on Φ_{CPA} can also be
143 noted. As the CPA radius gets larger, the J-aggregates have a smaller influence in the shape
144 of the modes and the intensity of the LP fades.

145 Since the QDs emission spectrum overlaps the UP and its lower tail overlaps the LP,
146 associating the PL at a given $E(k)$ with the emission of QDs or TDBC molecules is not
147 straightforward. Here again, we need a theoretical model to analyse these data and identify
148 the mechanisms responsible for the emission. We now describe the theoretical framework
149 that enables us to analyse the data and identify the emission mechanisms. As explained in
150 the next paragraph, a numerical simulation based on the local Kirchhoff's law enables to
151 explain the physical processes that contribute to the detected PL.

152 **Description of the theoretical model and comparison with the exper-**
 153 **iments**

154 The overall PL observed in Fig. 3 a-f results from the coupling of the fluorescent emitters
 155 (both QDs and TDBC molecules) to the electromagnetic modes (SPPs, UP, LP). It also
 156 depends on the possible energy transfer between QDs and molecules. Models of light emission
 157 must account for this interplay in order to accurately predict the spectrum and directions
 158 of emission. Here, we use the local form of Kirchhoff's law which enables to model light
 159 emission by nonequilibrium systems under some conditions.¹⁵

160 **Local form of Kirchhoff's law**

161 This law states that the power $dP_e^{(l)}(\mathbf{u}, \lambda)$ emitted by an ensemble of thermalized emitters
 162 at a wavelength λ , in the solid angle $d\Omega$ around the direction given by the unit vector \mathbf{u} and
 163 for a given linear polarization state l can be cast in the form:

$$dP_e^{(l)}(\mathbf{u}, \lambda) = d\lambda d\Omega \int_V d^3\mathbf{r}' \alpha^{(l)}(-\mathbf{u}, \mathbf{r}', \lambda) \frac{hc^2}{\lambda^5} \frac{1}{\exp(\frac{hc}{\lambda k_B T} - \frac{\mu(\mathbf{r}')}{k_B T}) - 1}, \quad (1)$$

164 where $\alpha^{(l)}(-\mathbf{u}, \mathbf{r}', \lambda) \varphi_{\text{inc}} d^3\mathbf{r}'$ is the absorption in a volume element $d^3\mathbf{r}'$ of the emitting
 165 material (QDs or TDBC molecules) illuminated by an incident plane wave coming from the
 166 reciprocal direction $-\mathbf{u}$ with a given linear polarization state l and a power flux per unit area
 167 φ_{inc} . T is the temperature and $\mu(\mathbf{r}')$ is the photon chemical potential. This quantity has
 168 been introduced in the context of semiconductor electroluminescence.²³ The photon chemical
 169 potential is then equal to the difference of the quasi Fermi levels in the valence band and the
 170 conduction band. In other words, the photon chemical potential is a characteristic of the
 171 strength of the pumping mechanism. It can be defined both for the QDs (μ_{QDs}) and for the
 172 molecules (μ_{Jagg}). It describes the number of excited emitters. It is thus a key quantity to
 173 study energy transfer between QDs and molecules. As it is shown in the Methods section,
 174 Eq. 1 can be cast in a simpler way, as a function of $\Delta\mu = \mu_{\text{QDs}} - \mu_{\text{Jagg}}$.

Eq. 1 shows that light emission $dP_e^{(l)}(\mathbf{u}, \lambda)$ is important when the absorptivity in the reciprocal picture $\alpha^{(l)}(-\mathbf{u}, \mathbf{r}', \lambda)$ is also significant. As a consequence, some of the spectral and spatial features observed in absorption measurements can be observed in light emission measurements. In particular, the influence of a SPP or a strongly coupled mode in the emission process is accounted for by this term.

The minima of reflectivity in Fig. 1c, are a clear signature of an increased absorptivity caused by the resonant excitation of the UP and LP. It directly matches the maxima of emission in Fig. 3a. Indeed, in the reciprocal picture, the system under pumping contains molecules or quantum dots that decay by emitting light through the same surface UP and LP. Similarly, Fig. 3f shows the same emission mediated by surface plasmons. It is seen that the formula accounts for both emission mechanisms mentioned above. On one hand, an excited QD has an emission tail at low frequencies that can excite either the LP or the SPP depending on its environment. This results in a significant emission due to the leakage radiation of the surface waves which is proportional to $\exp(\frac{\mu_{\text{QDs}}}{k_B T})$. On the other hand, the same QDs can transfer energy to the TDBC molecules. Then, a molecule emission proportional to $\exp(\frac{\mu_{\text{Jagg}}}{k_B T})$ mediated by leakage of the LP or SPP can be observed.

191 **The $\Delta\mu$ highlights the energy transfer between the two types of emitters**

Once the values for the refractive indexes of J-aggregated TDBC, bleached J-aggregated TDBC and QDs were extracted separately from the optimization procedure described in the Methods section, we computed the photoluminescence produced by the whole system (Fig. 1a, 2a). We can then compare Fig. 3a-f to numerical simulations (Fig. 3g-l).

It was necessary to adjust $\Delta\mu$ for each CPA to fit the relative intensities between the UP and LP branches. The data of $\Delta\mu$ are presented in table 1.

Table 1: Fitted values of $\Delta\mu = \mu_{\text{QDs}} - \mu_{\text{Jagg}}$

	unbleached	$\Phi_{\text{CPA}} = 1\mu\text{m}$	$\Phi_{\text{CPA}} = 2\mu\text{m}$	$\Phi_{\text{CPA}} \geq 5\mu\text{m}$
$\Delta\mu$ (meV)	270	291	295	μ_{QDs}

198 Since the QDs do not undergo any absorption-reemission process (See Methods section),
 199 we consider the laser spot as the only excitation source. Thus, the number of excited QDs,
 200 and hence μ_{QDs} , is the same for all CPA configurations. Consequently, a variation of $\Delta\mu$ can
 201 only be due to a variation of μ_{Jagg} , i.e. a variation of the number of excited J-aggregated
 202 molecules. The observed increase of $\Delta\mu$ when Φ_{CPA} is increased indicates a smaller number
 203 of excited TDBC molecules (i.e. a smaller μ_{Jagg}). These measurements are compatible with
 204 the picture of an energy transfer between the QDs and the J-aggregated molecules mediated
 205 by the SPPs propagating in the CPA. This process is suppressed if the SPP decay length is
 206 smaller than the CPA radius. Here, we find that for $\Phi_{\text{CPA}} \geq 5 \mu\text{m}$, the energy transfer is not
 207 measured. We evaluate the SPP intensity decay length to be around $2 \mu\text{m}$ (see Methods), a
 208 value consistent with the measurements. In this latter case, only the QDs contribute to the
 209 photoluminescent emission.

210 Interestingly, we also observe light emitted along the dispersion relation of the UP. This
 211 is not observed without QDs, as already reported in the literature.¹⁹ Here, the emission
 212 through the UP is due to the direct excitation of the UP electromagnetic mode by the QDs
 213 for the small values of Φ_{CPA} (see Fig. 3(a-b)). When Φ_{CPA} increases (see Fig. 3(e-f)), QDs
 214 emission is mediated by the SPP.

215 **PL emission out of the SPP, UP and LP modes**

216 Finally, we discuss the broad dispersion in $k_{//}$ of the emission seen in Fig. 3 b-e. It cannot
 217 be explained by invoking the sole dispersion relation of the polariton or the plasmons. The
 218 numerical simulations of Fig. 3 h-k show that the model is able to reproduce the experimental
 219 data so that this angular dependence is well captured by the sample absorptivity.

220 Here, we consider a particular pair $(E, k_{//})$ outside the upper polariton's dispersion re-
 221 lation in Fig. 4a), such as $E = 2.15 \text{ eV}$ and $k_{//} = 14 \mu\text{m}^{-1}$. A physical explanation of the
 222 broad dispersion in k can be provided by analysing the effect of the presence of a CPA in
 223 real space. According to Kirchoff's law, the emitted light is coming from regions where the

224 absorption proportional to $\text{Im}(\epsilon)|E|^2$ is large. We thus plot the field $|\vec{E}_z|$ in the structure
 225 when illuminated by an incident plane wave from the glass side towards the sample, with
 226 this specific energy and wave vector (corresponding to an angle of 58° , and a free-space
 227 wavelength $\lambda = 576.7$ nm) in Fig. 4. We investigate the field for the two cases in which
 228 a CPA of diameter $\Phi_{CPA} = 1 \mu\text{m}$ is present (Fig. 4b)) or absent (Fig. 4a)). We observe
 229 that when the J-aggregates are active everywhere, there is no coupling between the plane
 230 wave and any evanescent mode. In contrast, in the presence of a CPA of $\Phi_{CPA} = 1 \mu\text{m}$ the
 231 field is greatly enhanced. The CPA thus acts as an antenna, allowing to couple light in the
 232 structure for a wide range of excitation wavevectors. By reciprocity, the QDs excited in this
 233 spatial area where the field is non-zero are able to relax in the same range of wavevectors,
 234 as it is observed in the PL map of Fig. 3b. Physically these new wavevectors originate
 235 from the diffraction of surface plasmon polaritons on the edge of the bleached TDBC area.

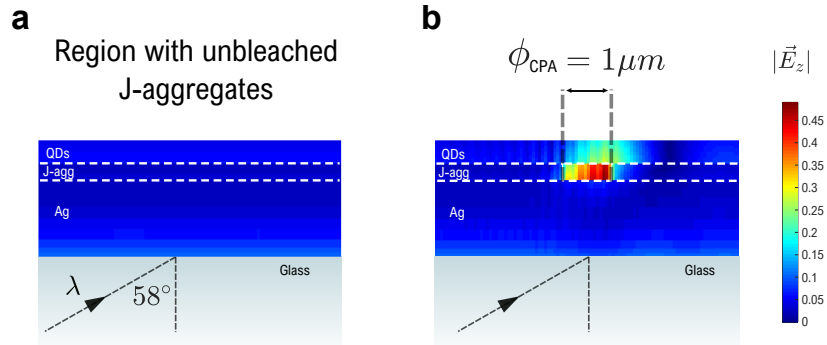


Figure 4: Maps of the field component \vec{E}_z norm produced by the incidence of a TM-polarized plane wave that illuminates the sample from the glass side, with a parallel wavevector $k_{//} = 14 \mu\text{m}^{-1}$ at 2.15 eV (i.e. at $\lambda = 576.7$ nm and for 58°). In a), a homogeneous region (i.e far from a CPA) is illuminated and there are no excited modes which explains that the field is zero. In b), the presence of the CPA enables the coupling of the plane wave producing an intense field in its vicinity.

236 Conclusion

237 In summary, we present an approach to characterize the PL and energy transfer in sys-
 238 tems with complex interactions between organic (J-aggregated TDBC) and inorganic (QDs)

239 emitters determined by light-matter coupling. By taking advantage of the microstructura-
240 tion of the organic layer, the electromagnetic environment created by the hybridization of
241 J-aggregates' emission and the SPP mode was probed with QDs as a function of the dis-
242 tance between emitters' ensembles. Microstructuration enables to target the QDs separately
243 while controlling the amount of active J-aggregates in the surroundings. This results in a
244 progressive tuning of both the shape of the propagating modes and the distribution of the
245 intensity among them. Surprisingly, we detect light emission in the UP mode contrarily
246 to what is normally observed in the absence of the QDs layer and also for large k-vectors
247 for which light emission is usually forbidden. Experimental observation are thoroughly un-
248 derstood thanks to a theoretical model involving a local form of the Kirchhoff's law that
249 introduces a spatial dependence of the photon chemical potential accounting for the pump-
250 ing of each active layer. Numerical simulations show the occurrence of a plasmon mediated
251 energy transfer over distances of several μm between spatially separated inorganic emitters'
252 ensembles and organic emitters' ensembles. The excellent agreement between model and
253 experiments, for any size of the CPA, shows that this comprehensive method enables the
254 interpretation of systems in which thermalized materials with different chemical potential
255 couple within complex structures. Our findings pave the way towards a thorough investiga-
256 tion of the interactions, mediated by the electromagnetic environment, between materials out
257 of thermodynamic equilibrium. This will open new avenues for the design and fabrication of
258 new materials bringing together the best of organic and inorganic worlds.

259 **Methods**

260 **Sample preparation**

261 The sample is fabricated as follows. First, a continuous 50 nm thick silver film is evaporated
262 onto a glass coverslip. Then, a layer of J-aggregates is deposited by spin-coating a solution
263 of 5,6-Dichloro-2-[[5,6-dichoro-1-ethyl-3-(4-sulfobutyl)-benzimi-dazol-2-ylidene]-propenyl]-1-

264 ethyl-3-(4-sulfobutyl)-benzimidazolium hydroxide, inner salt, sodium salt (TDBC) in dis-
 265 tilled water with a concentration of 8.6 mM. At this stage, we performed the UV-lithography
 266 to obtain circularly photobleached areas. Finally, we deposited on top a layer contain-
 267 ing CdSe core CdS/CdZnS/ZnS multishell QDs embedded in a transparent Poly(methyl
 268 methacrylate) (PMMA) matrix. For this layer, we prepare a solution of the QDs in toluene
 269 with a concentration of $\sim 1 \mu\text{M}$ in which transparent PMMA was added to the solution at a
 270 mass concentration of 0.5%. The solution was homogeneously deposited by spin coating and
 271 the QDs concentration was established so that the emitters are homogeneously dispersed in
 272 the layer. Note that the solvents are different for the J-aggregated TDBC and the QDs in
 273 order to avoid dissolving the first layer when the second layer is spin-coated. The thicknesses
 274 of the layers were determined by AFM topography measurements resulting in 17 nm for the
 275 TDBC J-aggregates and 15 nm for the QDs/PMMA layer.

276 **Theoretical model and simulations**

277 **Brendel-Bormann model for refractive indexes of fluorophores**

278 In order to describe the fluorophores' layers and compute the absorbed power and thus the
 279 photoluminescent emission (1), it is necessary to have a permittivity model for each layer of
 280 emitters that accounts for the inhomogeneous broadening of the transitions for each layer of
 281 emitters (see a discussion in ref²⁴). We use Brendel-Bormann models²⁵⁻²⁷ for each layer and
 282 adjust the parameters of the models by using the same procedure as the one described in
 283 ref.²⁴ The Brendel-Bormann expression is reminded below:

$$\epsilon(\omega) = \epsilon_{\text{bg}} + \sum_{k=1}^m X_k(\omega), \quad (2)$$

284 where X_k is an infinite sum of Lorentz oscillators whose amplitudes are given by a Gaussian
 285 function:

$$X_k(\omega) = \frac{1}{\sqrt{2\pi}\sigma_k} \int_{-\infty}^{+\infty} dx \exp\left(-\frac{(x - \nu_{0k})^2}{2\sigma_k^2}\right) \frac{\nu_{\text{pk}}^2}{x^2 - \omega^2 - i\nu_{\text{rk}}\omega}. \quad (3)$$

286 To find the parameters of the J-aggregated TDBC model of permittivity, we use the
 287 photoluminescent map from the system made of the silver and molecules layers, before the
 288 bleaching and before the QDs' deposition. The experimental data as well as the parameters
 289 of the model are identical to the parameters used in ref.²⁴ The TDBC layer displays some
 290 anisotropy, so that we introduce the refractive index of the molecules in the perpendicular
 291 direction of the layer (denoted n_{\perp}) as an additional constant parameter of the cost function
 292 $f_{\text{cost}}(\epsilon)$ (see ref.²⁴).

293 We model the CPA by a medium of homogeneous refractive index within the bleached
 294 region. The index model is chosen as dispersion free, and does not display any excitonic
 295 transition. The permittivity model of both CPA and QDs are determined at the same time
 296 by an optimization process based on the fit of the photoluminescent map given in Fig. 3f,
 297 where the QDs are deposited on an infinite layer of bleached J-aggregated TDBC.

298 Before performing the optimization procedure, we first filter some noise by convoluting
 299 by a rectangular window function in the (λ, θ) plane whose widths are 6.2 nm and 2°. The
 300 values of the parameters are gathered in table 2.

Table 2: Brendel-Bormann model parameter values

Parameters	J-aggregates			bleached J-aggregates	QDs	
	k=1	k=2	k=3		k=1	k=2
ν_{0k} (eV)	2.07	2.14	2.17	/	2.22	2.76
$\nu_{\tau k}$ (eV)	1.14e-09	1.46e-13	2.10e-06	/	3.83e-12	3.72e-11
ν_{pk} (eV)	0.10	1.44	0.25	/	0.013	0.83
σ_k (eV)	0.025	0.025	0.070	/	0.042	0.13
ϵ_{bg}		2.83		2.13	3.18	
n_{\perp}		2.82		/	/	

301 **Approximations in the local Kirchhoff's law**

302 Two approximations of Eq.1 have been made to compute the PL of Fig. 3 g-l. Firstly, $\mu(\mathbf{r}')$
 303 was considered to be a non-zero constant in the volume of excited emitters and zero every-
 304 where else, as can be shown in Fig. 2b, where the hatched areas correspond to the volumes

305 of excited emitters.

306 Let us first discuss the volume of emitting QDs. Experimentally, the excitation laser fre-
307 quency was selected to pump preferentially the QDs. The volume of excited QDs is thus
308 defined by the laser spot size, here a disk of diameter $\Phi_{\text{QDs}} = 500 \text{ nm}$. We verified that the
309 quantum dots cannot be re-excited by the surface plasmon launched by the QDs at 570 nm
310 (the QDs' emission wavelength). To do that, we consider the system described in Fig. 1a
311 and 3f, when the TDBC layer is entirely bleached. We compare the intensity decay length
312 of the plasmon (defined as $1/(2k'')$) with and without the QDs. If the decay length does not
313 change significantly, most of the absorption is due to the metal so that multiple absorption-
314 emission processes cannot take place. In other words, we compute the decay length of the
315 surface plasmon when the QDs' layer is described by a BB refractive index described in
316 Table 2. We obtain $\delta_1 = 2.21 \mu\text{m}$. We then discard the resonance of the QDs by replacing
317 its refractive index by its background contribution only i.e. $n_{\text{BQbg}} = 1.78$. The decay length
318 slightly increases to $\delta_2 = 2.36 \mu\text{m}$ without the absorption of the QDs. This tiny increase
319 of the decay length points out that the absorption by the QDs is too low to display any
320 absorption - re-emission process. The QDs are thus only excited in the volume defined by
321 the laser spot size.

322 Regarding the volume of excited J-aggregated TDBC molecules, it was defined following
323 observations and interpretations from the experimental data from Fig 3b-f. In these cases,
324 the molecules are photobleached over areas larger than Φ_{QDs} (except for Fig 3a and 3g),
325 and can be excited directly neither by the QDs nor by the excitation laser. *However, it was*
326 *necessary to include a nonzero chemical potential for the molecules to reproduce theoretically*
327 *the experimental data of light emission in Fig. 3g-i. We interpret this observation by consid-*
328 *ering that the J-aggregated molecules are excited by the QDs through the surface plasmons.*
329 In a rigorous manner, we should take into account all the J-aggregated molecules outside
330 the bleached area. However, for numerical computation, we had to take into account a finite
331 volume of diameter Φ_{Jagg} of excited molecules, where we consider that all the molecules are

332 excited inside and none outside ($\mu_{\text{Jagg}}(\rho) = 0$ for $\rho > \Phi_{\text{Jagg}}/2$, Fig. 2b). We identify 3
 333 different cases :

- 334 1. The case where the QDs are deposited on top of an infinite layer of active J-aggregated
 335 molecules (Fig. 3a). In that case, $\Phi_{\text{Jagg}} = 2\delta_a$, where $\delta_a = 1.21 \mu\text{m}$ is the intensity
 336 decay length of the upper polariton at 570 nm.
- 337 2. The case where the molecules are photobleached over areas larger than Φ_{QDs} , with
 338 $\Phi_{\text{CPA}} < 2\delta_1$ (Fig 3 b-c), with $\delta_1 = 2.21 \mu\text{m}$ defined earlier as the decay length of
 339 the surface plasmon at 570 nm, launched by the QDs on top of a bleached area of
 340 molecules. In that case, $\Phi_{\text{Jagg}} = 2(R_{\text{CPA}} + \delta_a)$.
- 341 3. For configurations where the CPA is larger than $2\delta_1$ (Fig 3 d-f with $\Phi_{\text{CPA}} = 5, 8$
 342 and $40 \mu\text{m}$, respectively), we could recover the experimental data without including a
 343 contribution of the molecules so that $\Phi_{\text{Jagg}} = 0$.

344 This choice of effective volume with a constant value of μ_{Jagg} is equivalent to the compu-
 345 tation of the absorption over the entire volume when assuming that the number of excited
 346 molecules decays exponentially as $\frac{1}{r} \exp(-r/\delta_a)$.

347 The values of the diameter Φ_{Jagg} of the volume of excited TDBC are presented in table 3.

Table 3: Values of the effective diameters Φ_{Jagg}

	unbleached	$\Phi_{\text{CPA}} = 1 \mu\text{m}$	$\Phi_{\text{CPA}} = 2 \mu\text{m}$	$\Phi_{\text{CPA}} \geq 5 \mu\text{m}$
$\Phi_{\text{Jagg}} (\mu\text{m})$	2.4	3.4	4.4	0

348 Finally, the Wien's approximation is valid at 300K and states that $\exp(\frac{h\omega - \mu(\mathbf{r}')}{k_B T}) \gg 1$
 349 and the medium is considered homogeneous over the entire volumes of the different layers,
 350 and defined by its temperature T .

351 With these assumptions, Eq. (1) can be simplified and rearranged as the sum of the two
 352 contributions due to the QDs and the molecules. We remind that the molecules are placed

353 between the silver layer and the QDs layer. We obtain :

$$dP_e^{(l)}(\mathbf{u}, \lambda) = d\lambda d\Omega [dP_{\text{abs}}^{\text{Jagg}}(-\mathbf{u}, \lambda) I_{\text{BB}}(\lambda) e^{\frac{\mu_{\text{Jagg}}}{k_B T}} + dP_{\text{abs}}^{\text{QDs}}(-\mathbf{u}, \lambda) I_{\text{BB}}(\lambda) e^{\frac{\mu_{\text{QDs}}}{k_B T}}], \quad (4)$$

354 with

$$dP_{\text{abs}}^i(-\mathbf{u}, \lambda) = \varphi_{\text{inc}} \int_{V_i} d^3\mathbf{r}' \alpha^{(l)}(-\mathbf{u}, \mathbf{r}', \lambda), \quad (5)$$

355 and

$$I_{\text{BB}}(\lambda) = \frac{1}{\lambda^5} \frac{1}{\exp\left(\frac{hc}{\lambda k_B T}\right)}. \quad (6)$$

356 After factorisation and normalization by the maximum emitted power at λ_0 and \mathbf{u}_0 , Eq.
357 4 becomes:

$$\frac{dP_e^{(l)}(\mathbf{u}, \lambda)}{dP_e^{(l)}(\mathbf{u}_0, \lambda_0)} = \frac{I_{\text{BB}}(\lambda)}{I_{\text{BB}}(\lambda_0)} \frac{dP_{\text{abs}}^{\text{Jagg}}(-\mathbf{u}, \lambda) + dP_{\text{abs}}^{\text{QDs}}(-\mathbf{u}, \lambda) e^{\frac{\Delta\mu}{k_B T}}}{dP_{\text{abs}}^{\text{Jagg}}(-\mathbf{u}_0, \lambda_0) + dP_{\text{abs}}^{\text{QDs}}(-\mathbf{u}_0, \lambda_0) e^{\frac{\Delta\mu}{k_B T}}}, \quad (7)$$

358 with $\Delta\mu = \mu_{\text{QDs}} - \mu_{\text{Jagg}}$. This factor $\Delta\mu$ is adjusted to fit the experimental emission.

359 For $\Phi_{\text{CPA}} > 2\delta_1$, $\Delta\mu = \mu_{\text{QDs}}$ and $dP_{\text{abs}}^{\text{Jagg}}(-\mathbf{u}, \lambda)$ is null. Only the QDs contribute to the
360 photoluminescent emission in this latter case.

361 Thicknesses identification

362 Once refractive indexes for J-aggregated TDBC, bleached J-aggregated TDBC and QDs are
363 extracted from the optimization procedure for each type of emitters separately, it is possible
364 to compute the emission of the whole system composed of QDs on active and bleached
365 J-aggregated TDBC, on top of the silver layer.

366 We used the system without bleached molecules (Fig. 3g) to adjust the thickness of the
367 different layers to fit the experimental branches positions. We found $t_{\text{Jagg}}^{\text{th}} = 11$ nm and $t_{\text{QDs}}^{\text{th}} =$
368 15 nm, which is consistent with the experimental atomic force microscopy measurements
369 ($t_{\text{Jagg}} = 17$ nm and $t_{\text{QD}} = 15$ nm). These values were kept the same for all CPA configurations

370 (Fig 3h-l, matching Fig 3b-f).

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460 TOC Graphic

For Table of Contents Use Only
 Title: "Plasmon mediated energy transfer between two systems out of equilibrium"
 Authors: Camilo R. Pérez de la Vega, Elise Bailly, Kévin Chevrier, Benjamin Vest, Jean-Paul Hugonin, Antoine Bard, Alban Gassenq, Clémentine Symonds, Jean-Michel Benoit, Joel Bellessa, Jean-Jacques Greffet, Yannick De Wilde, Valentina Krachmalnicoff.

461

Synopsis: This graphic depicts a multi-layered sample composed of a glass substrate with a silver film, a layer of J-aggregates, and a layer of quantum dots deposited on it. When a blue laser is directed through the substrate towards a region of the sample where the J-aggregates have undergone photobleaching, the quantum dots layer is excited. Energy transfer between quantum dots and J-aggregates mediated by surface plasmon polaritons can be studied by taking advantage of the microstructuration of the multilayered sample.

