Photophysics

DOI: 10.1002/ange.200903191

Molecule–Light Complex: Dynamics of Hybrid Molecule–Surface Plasmon States**

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Charge transfer complexes, in which the molecules interact by sharing electrons giving rise to new molecular states, are well known. The interaction force between the molecules is mediated by the exchange of electrons. Perhaps less well known, but in close analogy, is the fact that molecules can interact with an electromagnetic field by the exchange of photons, leading to new hybrid states. Such strong interaction can occur when the field has discrete energies just like the molecule. In this case, the molecule and the field modes may interact like any two systems as shown in Figure 1 which is reminiscent of two atomic orbitals coupling to give new molecular states.

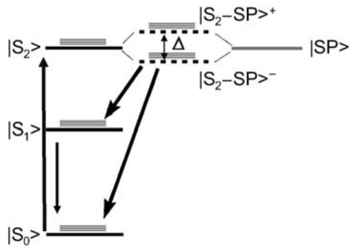

Figure 1. Molecular state diagram showing the ground state $|S_0>$, two excitonic states $|S_1>$ and $|S_2>$ and the formation of hybrid states due to strong coupling between an SP resonance and $|S_2>$. The hybrid states $|S_2\text{-SP}>^+$ and $|S_2\text{-SP}>^-$ are separated by the Rabi splitting Δ. They may open up different relaxation pathways after photoexcitation and lead to new chemistry.

The question that then naturally arises from a chemist point of view is what are the properties of such molecular -light "complexes"? Can they be used to modify any physical or chemical property of the molecule as in the case of exciplexes or excimers? To answer such questions, we need to be able to prepare these species in a relatively simple way and then to identify spectroscopically the hybrid states generated by the interaction with light and probe their properties. As discussed below, recent developments in the area of surface plasmons makes the preparation much easier and as we show herein, enables the first steps to be made in the exploration of the properties of these molecular–light complexes.

Traditionally the generation of hybrid states between matter and the electromagnetic modes, known as strong coupling, was achieved by placing, for instance, a semiconducting material in an appropriately tuned optical cavity such as defined by two mirrors. Such systems have been studied extensively both theoretically and experimentally.[1] The observed splitting between the coupled states (see Figure 1), known as the Rabi splitting, is twice the interaction energy. Molecules can also be observed to undergo strong coupling with light in cavities[2] or with surface plasmons. We recall that surface plasmons can be thought of as light trapped at the surface of a metal and give rise to intense local electromagnetic fields. Strong coupling between surface plasmons (SPs) and molecules was first studied in the 1970's.[3] More recently, we and others confirmed that such coupling could indeed take place and there have been many studies in this direction.[4] Hole arrays in metallic films are particularly useful for the purpose of the present study since they have tunable SP resonances which also give rise to enhanced transmission.[5] They can be coated with molecules and be placed, instead of optical cells, in any standard spectroscopic apparatus such as a spectrophotometer or a transient spectroscopy set-up.[6,7] Below we use such structures to gain new insight in the properties of the hybrid states.

For the present study, hole arrays were milled by focused ion beam in Ag films deposited on quartz slides (see insert in Figure 2). For the molecular material, we chose the J-aggregate of H_4TPPS (acidic form of the tetraphenyl porphyrin tetrasulfonate) dispersed in PVA (polyvinyl alcohol) which was spin-coated on the array. J-aggregates have the advantage of having sharp absorption peaks with very high absorption coefficients corresponding to the S_1 and S_2 exciton states (Figure 2b). Such feature is particularly suitable for strong coupling. The photophysical properties of these aggregates have been well studied.[8,9]

The evidence for strong coupling between molecules and the SP field is typically verified by doing a number of different static measurements. The most standard verification is the opening of a gap (Rabi splitting) in the dispersion (energy versus momentum) curve of the SP at the energy of the molecular absorption transition. The splitting must be larger than the width of the absorption peak and the coupled optical mode, and it depends on the square root of the concentration of molecules in the electromagnetic field. Such measurements have all been performed for this system and will be detailed elsewhere.[10] Here we prefer to focus on the main points relevant to the dynamic results presented below.

Figure 2a illustrates the transmission spectrum of hole array in the absence of the J-aggregates. Each peak is associated with an SP resonance whereby the electromagnetic

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[**] This work has been funded by the French Agence Nationale de la Recherche under contract ANR 06-BLAN-0275.

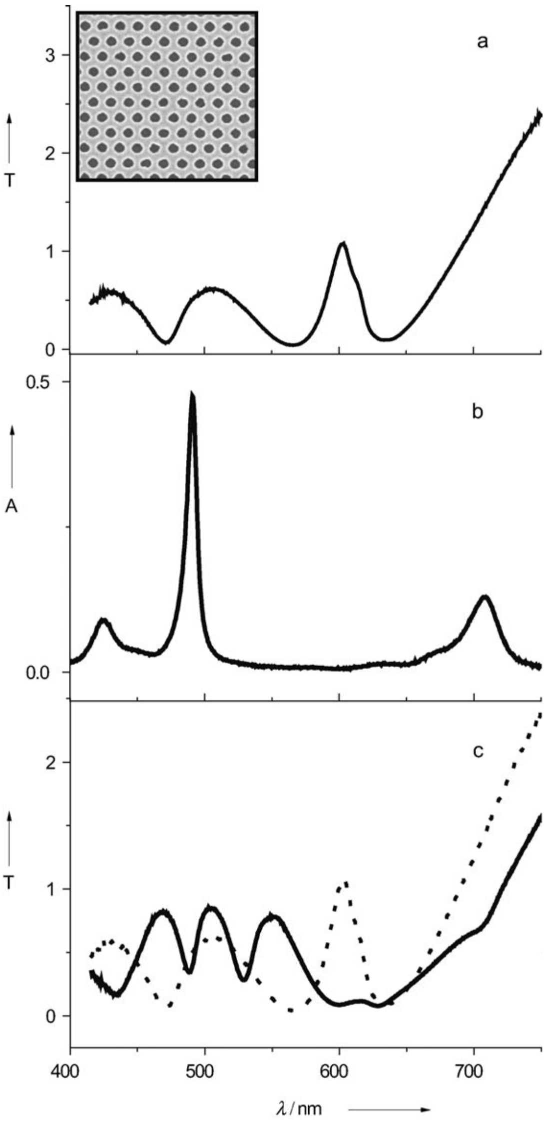

Figure 2. a) Transmission spectrum of an hexagonal hole array in a 100 nm thick Ag film spin-coated with a PVA layer of about 150 nm. The transmission was measured with collimated white light at normal incidence. The array periodicity is 480 nm with hole diameter of about 230 nm. Inset: a scanning electron microscope (SEM) image of part of the hole array. b) The absorbance spectrum of H_4TPPS J-aggregates in PVA spin-coated onto a quartz substrate. The peak positions of the S_1 and S_2 exciton bands are at 706 nm and 490 nm, respectively. The peak at 420 nm is the monomer residue. c) Transmission spectrum of the hole array covered with the J-aggregate PVA film (solid trace). The spectrum clearly shows the formation of a new mix state at 525 nm as discussed in the text. The dotted line is the same transmission spectrum as in (a).

field becomes intense at the metal interface. The position of the SP resonances, and therefore of the transmission peaks, are given in a first approximation by the following equation for an array with hexagonal symmetry:[6]

$$\lambda_{\max} = \frac{P}{\sqrt{\frac{4}{3}(i^2 + i,j + j^2)}}\sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}} \qquad (1)$$

where ε_m and ε_d are respectively the dielectric constants of the metal and the dielectric material in contact with the metal, (i,j) the scattering orders and P the periodicity of the array.

It is important to note that both interfaces of the metal film can support SP resonances and that these can in turn interact, modifying their energies which is the case in this experiment, specially because the metal film was kept thin to facilitate the transient spectroscopy study. In the array of Figure 2 a, the period (480 nm) was chosen in order that one of the resonances (i,j: 2,0) overlaps with the strong S_0 to S_2 excitonic transition of the J-aggregates around 490 nm (shown in Figure 2 b) and to give rise to the strongest coupling intensity. This combination splits the SP transmission resonance of the array into three peaks as can be seen in Figure 2 c due to the threefold degeneracy of the SP resonance, a direct consequence of the triangular symmetry of the hole array. The complexity of the splitting precludes a simple determination of the exact gap of the hybrid states but the separation of the peaks is on the order of 200 meV for the concentration of J-aggregate used in the PVA film (ca. 3×10^{-2} M), typical value observed for molecular strong coupling.[2,4]

The static transmission peaks of the molecule–hole array combination (of Figure 2 c) only reveals the strong interaction and its associated energy but tell us nothing about the nature of these hybrid states. The latter must have electronic as well as plasmonic character so that they should be apparent in the absorption spectra of the ground state and one should be able to populate them transiently. Nevertheless, extracting the absorption spectrum of the molecule–SP complex from the static transmission of the hole array in the presence and absence of J-aggregates (i.e. from the two spectra in Figure 2 c) is extremely difficult because of the coupling and the presence of the strong absorption band of the molecule at high concentrations induces a local change in the refractive index (i.e. Kramers–Kronig relations)[11] which in turn shifts the SP related transmission peaks as expected from Equation (1) and observed experimentally.[7,11] The great advantage of transient absorption spectroscopy is that it can measure small absorbance *changes* which as consequence perturb the index of the J-aggregate/PVA film very little. In such conditions, the transient spectrum of the molecules on the hole array reflects the difference in the absorption spectra of the ground state and the excited states generated and therefore should provide information on the existence of hybrid states.

To verify this, various samples were analyzed with a 150 fs pump–probe laser setup (ca. 0.3 mJ cm^{-2} per pulse at 400 nm). The transient differential absorption spectra recorded immediately after excitation at 400 nm are plotted in Figure 3. The first spectrum is that of the J-aggregate film in the absence of a hole-array in good agreement with that reported in the literature[9] with the dips at 490 nm and 700 nm due to the depopulation of the ground state and, in between, a broad positive maximum due to the absorption of the populated state to higher excited states. The next spectra are recorded for samples with different hole-array periods to move an SP resonance gradually into coincidence with the S_0 to S_2 transition. As the period increases, strong new spectral

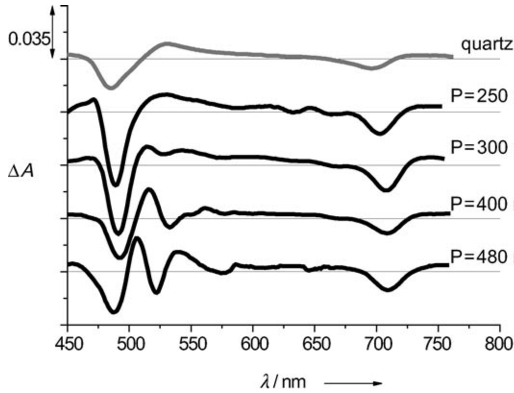

Figure 3. Transient absorption spectra of H_4TPPS J-aggregates in PVA spin-coated onto different substrates: quartz and Ag hexagonal hole arrays with periodicities of 250, 300, 400, and 480 nm as indicated in the figure. The spectra were taken immediately after the 150 fs pulse. They have been corrected for chirping and smoothed.

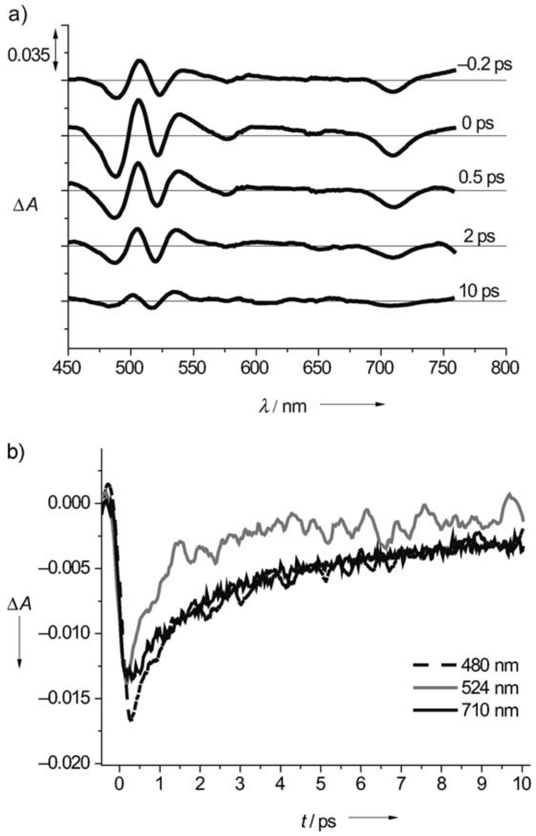

Figure 4. a) Transient spectra recorded at different times after excitation at 400 nm of the J-aggregates (H_4TPPS) in PVA spin coated onto big hole array with 480 nm periodicity (blue curve of Figure 3). They have been corrected for chirping and smoothed. b) Kinetic traces at 480, 524, and 710 nm.

features appear near this transition at longer wavelengths. These features occur exactly at the wavelengths where the strong coupling is apparent in the static experiments (Figure 2c). It also worth noting that there are no new spectral features at the S_0 to S_1 absorption peak around 700 nm as expected since this transition is only weakly coupled to a broad SP resonance (small absorption dip in solid trace of Figure 2c). The negative dip around 525 nm (for period: 480 nm) must be due to a strong positive absorption at this wavelength in the ground state spectrum of the molecule-SP complex corresponding to the transition from S_0 to the $|S_2\text{-SP}>^-$ state. The latter lies ca. 170 meV below S_2, giving again an estimation of the Rabi splitting in agreement with the static measurements. From the relative intensities of the dips at 525 nm (S_0 to $|S_2\text{-SP}>^-$) and at 490 nm (S_0 to S_2), it is clear that not all the molecules are strongly coupled and that the S_0 to $|S_2\text{-SP}>^-$ absorption coefficient (transition probability) is high. Next we study the relaxation dynamics of the different spectral features for the same strong coupling conditions.

Figure 4 shows the temporal evolution of the transient spectrum together with the kinetics at three different wavelengths corresponding to three negative dips in the transient spectrum. With deconvolution for pulse width, a rapid decay with a half-life of 700 fs is seen around the dip at 525 nm. Simultaneously a small growth can be seen at 700 nm. The transient spectrum continues to evolve with a slower decay having a half-life of ≈2.5 ps followed by a component having a half-life of ca. 30 ps. These are the same as those of the J-aggregate/PVA film alone. When the sample is excited at 690 nm, the spectra and decay are essentially the same except for the first fast 700 fs relaxation which is no longer present. We attribute the fast component, most easily observed at 525 nm, to the lifetime of the hybrid $|S_2\text{-SP}>^-$ state. It is populated by the excitation at 400 nm. The $|S_2\text{-SP}>^-$ state then decays partially at least to S_1 explaining the small growth at 700 nm observed immediately after the pulse. The subsequent decays which occur also in the absence of strong coupling have been studied in detail by others.[9] The 2.5 ps decay has been attributed to vibrational cooling of the S_1 state and probably explains small spectral shifts occuring in the first picoseconds (see Figure 4a) while the longuest component is the lifetime of the S_1 exciton in the conditions of our film. These spectral and dynamic results are quite different from another study involving H_4TPPS–surface plasmon strong coupling, probably due to the different configuration of the experiment.[4d]

Many studies over the past 30 years have shown that the high fields of the SPs can enhance photophysical and photochemical processes.[12–21] This is typical of surface enhanced Raman or photopolymerization where the metallic structure acts to concentrate the electromagnetic field much like a lens focusing light. While such uses of SPs are interesting in themselves, these processes are in what one would call the weak coupling regime where the molecular states are essentially those of the isolated molecules.

Such SP enhanced phenomena must not be confused with the strong coupling regime studied here where new hybrid states between molecules and SPs are formed. The SPs provide a convenient way to prepare and control the molecule–light complexes. It is clear that transient absorption spectroscopy is ideally suited to study strong coupling. For instance, a new negative absorption peak in the differential spectrum can only be the result of a transition from the ground to the hybrid state, providing unambiguous signatures of strong coupling, in the same way as photoluminescence experiments.[1d,4e] The hybrid molecule–SP states can be clearly identified and populated with lifetimes comparable to the pure molecular excitonic states, providing a new channel for relaxation or chemical events. The properties of the molecule–light complexes are reminiscent of exciplexes and hence such species should perhaps be named photoplexes. By their intrinsic nature, the energies of these photoplexes can be tuned both via the surface plasmon resonance frequency as well as the concentration for the molecules, the symmetry of the structure and the polarization of the light. Such unique features should offer many possibilities for modifying photophysical and photochemical, and perhaps even chemical, properties of molecules. We expect more findings on such molecule–light complexes in the future.

Received: June 12, 2009
Revised: July 15, 2009

Keywords: photophysics · porphyrinoids · strong coupling · surface plasmon resonance · transient spectroscopy

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[1] a) C. Weisbuch, M. Nishioka, A. Ishikawa, Y. Arakawa, *Phys. Rev. Lett.* **1992**, *69*, 3314–3317; b) R. Houdré, C. Weisbuch, R. P. Stanley, U. Oesterle, P. Pellandini, M. Ilegems, *Phys. Rev. Lett.* **1994**, *73*, 2043; c) M. S. Skolnick, T. A. Fisher, D. M. Whittaker, *Semicond. Sci. Technol.* **1998**, *13*, 645–669; d) R. Houdré, *Phys. Status Solidi B* **2005**, *242*, 2167–2196.

[2] D. G. Lidzey, D. D. C. Bradley, M. S. Skolnick, T. Virgili, S. Walker, D. M. Whittaker, *Nature* **1998**, *395*, 53–55.

[3] a) V. M. Agranovich, A. G. Malshukov, *Opt. Commun.* **1974**, *11*, 169–171; b) P. G. Sherman, M. R. Philpott, *J. Chem. Phys.* **1978**, *68*, 1729–1735; c) I. Pockrand, A. Brillante, D. Möbius, *J. Chem. Phys.* **1982**, *77*, 6289–6295.

[4] a) J. Bellessa, C. Bonnand, J. C. Plenet, J. Mugnier, *Phys. Rev. Lett.* **2004**, *93*, 0364404; b) J. Dintinger, S. Klein, F. Bustos, W. L. Barnes, T. W. Ebbesen, *Phys. Rev. B* **2005**, *71*, 035424; c) Y. Sugawara, T. A. Kelf, J. J. Baumberg, M. E. Abdelsalam, P. N. Bartlett, *Phys. Rev. Lett.* **2006**, *97*, 266808; d) G. P. Wiederrecht, J. E. Hall, A. Bouhelier, *Phys. Rev. Lett.* **2007**, *98*, 083001; e) C. Symonds, C. Bonnand, J. C. Plenet, A. Bréhier, R. Parashkov, J. S. Lauret, E. Deleporte, J. Bellessa, *New J. Phys.* **2008**, *10*, 065017.

[5] T. W. Ebbesen, H. J. Lezec, H. F. Ghaemi, T. Thio, P. A. Wolff, *Nature* **1998**, *391*, 667–669.

[6] C. Genet, T. W. Ebbesen, *Nature* **2007**, *445*, 39–46.

[7] J. Dintinger, I. Robel, P. V. Kamat, C. Genet, T. W. Ebbesen, *Adv. Mater.* **2006**, *18*, 1645–1648.

[8] P. G. Van Patten, A. P. Shreve, R. J. Donohoe, *J. Phys. Chem. B* **2000**, *104*, 5986–5992.

[9] H. Kano, T. Kobayashi, *J. Chem. Phys.* **2002**, *116*, 184–195.

[10] A. Salomon, C. Genet, T. W. Ebbesen, in preparation.

[11] J. Dintinger, S. Klein, T. W. Ebbesen, *Adv. Mater.* **2006**, *18*, 1267–1270.

[12] D. Jeanmaire, R. Van Duyne, *J. Electroanal. Chem.* **1977**, *84*, 1–20.

[13] A. Nitzan, L. E. Brus, *J. Chem. Phys.* **1981**, *74*, 5321–5322.

[14] C. J. Chen, R. M. Osgood, *Phys. Rev. Lett.* **1983**, *50*, 1705–1708.

[15] J. S. Suh, N. H. Jang, D. H. Jeong, M. Moskovits, *J. Phys. Chem.* **1996**, *100*, 805–810.

[16] R. C. Jin, Y. W. Cao, E. C. Hao, G. S. Metraux, G. C. Schatz, C. A. Mirkin, *Nature* **2003**, *425*, 487–490.

[17] S. Kühn, U. Hakanson, L. Rogobete, V. Sandoghdar, *Phys. Rev. Lett.* **2006**, *97*, 017402.

[18] L.-Q. Chu, R. Förch, W. Knoll, *Angew. Chem.* **2007**, *119*, 5032–5035; *Angew. Chem. Int. Ed.* **2007**, *46*, 4944–4947.

[19] I. Lieberman, G. Shemer, T. Fried, E. D. Kosower, G. Markovich, *Angew. Chem.* **2008**, *120*, 4933–4935; *Angew. Chem. Int. Ed.* **2008**, *47*, 4855–4857.

[20] A. Blesso, W. Qian, M. A. El-Sayed, *J. Am. Chem. Soc.* **2008**, *130*, 3258–3259.

[21] A. Blesso, W. Qian, X. Huang M. A. El-Sayed, *J. Am. Chem. Soc.* **2009**, *131*, 2442–2443.