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Singlets and triplets in hybrid nanodevices

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An organic material thin layer can be used to resonantly absorb light and nonradiatively transfer excitation to an adjacent inorganic quantum well the optical nonlinearities of which can in this way be turned on more efficiently than by direct optical pumping. We theoretically consider this process in a hybrid structure based on crystalline tetracene in which the singlet exciton energy is close to twice the one of a triplet exciton and thermally activated singlet exciton fission into two triplets can be efficient. We investigate how the temperature dependence of the singlet exciton diffusion length affects the functional properties of such hybrid organic-inorganic nanostructures based on tetracene. We show how temperature activated fission opens a new possibility to turn on and off the indirect pumping due to energy transfer from the organic into the inorganic subsystem.

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Introduction. Combining inorganic and organic semiconductors in a single nanostructure is a promising route to stretch the rules that govern the light-matter interaction and improve the functional properties of devices. Much theoretical and experimental progress has been made in the last years as discussed in the recent review [1], and references therein. Yet, the giant optical nonlinearities anticipated for hybrid Frenkel–Wannier excitons in strongly coupled organic-inorganic heterostructures have not been experimentally observed so far. The weak coupling regime in which Frenkel and Wannier excitons maintain their individuality, but can irreversibly exchange excitation energy via the non-radiative dipole-dipole interaction is much more easily accessible experimentally. The strong optical nonlinearities [2] typical of the large radius Wannier exciton can be efficiently turned on via excitation energy transfer from the Frenkel excitons that due to their large oscillator strength may efficiently act as a light harvesting subsystem, as we have very recently discussed for a hybrid nanostructure based on anthracene and on a II–VI inorganic semiconductor quantum well [3].

Here, we consider as organic material a thin layer of tetracene showing that it gives in some conditions a strong pumping of the quantum well, but also the possibility to control the pumping efficiency varying the sample temperature. As a matter of fact, aside from the pumping intensity, the indirect pumping rate crucially depends on the singlet exciton diffusion length which in a material like tetracene is strongly temperature dependent due to the activation of fission processes whereby one singlet exciton turns into two triplets excitons having a slightly higher total energy [4]. While exciton fission can be beneficial in photovoltaic devices providing a higher yield of charge carriers [5], its role on the energy transfer process in a hybrid structure as sketched in Fig. 1 has not been addressed before. In the tetracene overlayer (having thickness L and absorption coefficient α) Frenkel excitons are generated by optical pumping and diffuse to the organic-inorganic interface, whereupon they non-radiatively transfer (with effective Förster radius R_0 [3]) to the inorganic semiconductor subsystem of thickness W comprising a II–VI quantum well and its thin barriers. Note that the energy of each triplet exciton is too low to allow for energy transfer in this case. The indirect pumping of the quantum well and the turning on of its optical nonlinearities can be very efficient provided $R_0 \sim W \ll L \sim \alpha^{-1} < L_D(T)$, being $L_D(T)$ the temperature dependent diffusion length which takes into account singlet exciton fission processes. We calculate here in detail the efficiency of such indirect optical pumping in a tetracene based hybrid heterostructure assuming for illustrative purposes values of inorganic material parameters appropriate for II–VI inorganic semiconductors. As a results of such non-radiative energy transfer the inorganic quantum well

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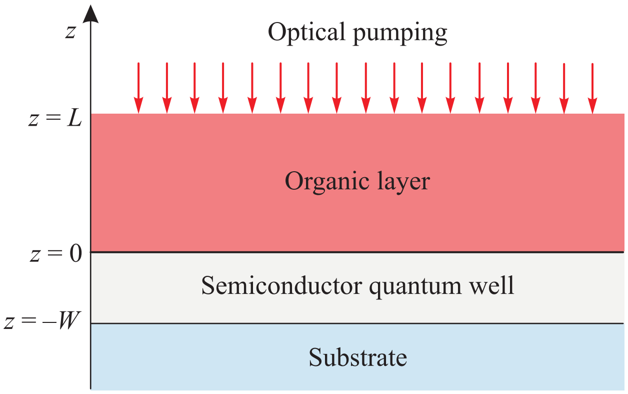

Fig. 1. (Color online) Sketch of the hybrid heterostructure made of an inorganic II–VI quantum well in close proximity with a thin tetracene overlayer. The light absorption in the latter can be much larger than the direct absorption by the quantum well so that tetracene plays the role of a funnel of pumping radiation energy, provided exciton diffusion and nonradiative energy transfer are efficient enough

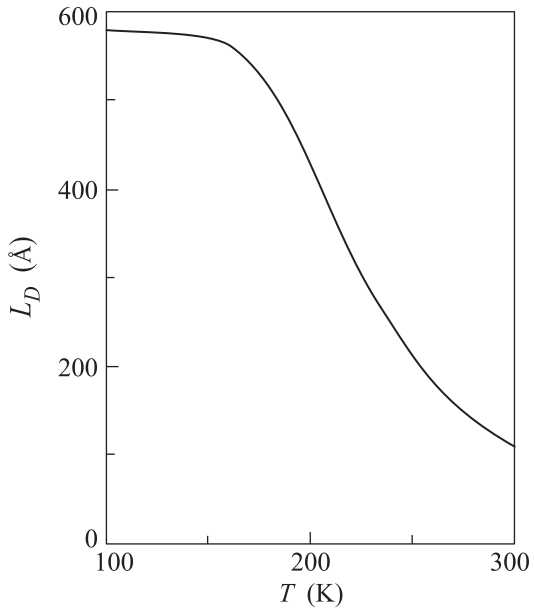

Fig. 2. Temperature dependence of the singlet exciton diffusion length in tetracene (adapted from Ref. [6])

can achieve a high excitation density and thus exhibit a number of nonlinear optical effects which have attracted much attention [2]. The material parameters describing tetracene, and in particular the role of the thermally activated singlet exciton fission into two triplets, are taken to be definite from the experimental study by Vaubel and Baessler [6] carried out in a wide range of temperatures. Differently from the case of anthracene, fission of a singlet tetracene exciton into a pair of triplet excitons reduces the singlet exciton life-time and for this reason the singlet exciton diffusion length is strongly temperature dependent. This, in turn, opens the possibility of an unusual temperature dependence of the energy transfer behavior from the tetracene thin layer to the quantum well, which is the focus of the present work.

Tetracene crystal as organic layer in an hybrid structure. As organic subsystem in the hybrid structure we consider a thin layer of crystalline tetracene. The diffusion length L_D of singlet excitons in crystalline tetracene at room temperature is $L_D = 120 \pm 10$ Å. It increases exponentially with decreasing temperature until it approaches a constant value of $L_D = 580 \pm$ $\pm\ 50$ Å below 190 K. The temperature dependence of the singlet exciton lifetime τ determined by exciton fission into two triplet excitations can fully account for the observed temperature dependence of the diffusion length [6]. In fact, the exciton diffusion coefficient in crystalline tetracene is $D = L_D^2/\tau = 3.3 \cdot 10^{-3}\,\mathrm{cm^2\,s^{-1}}$ and it is with high accuracy independent of temperature. The temperature dependence of L_D in tetracene is shown in Fig. 2 (adapted from Ref. [6]). We will argue that such dependence of the diffusion length on temperature leads to the possibility to turn on or off the indirect pumping of the II–VI quantum well via energy transfer from the tetracene layer in the hybrid nanostructure of Fig. 1. To undergo fission the exciton singlet in tetracene needs to obtain an additional energy of about 0.175 eV [6] from the interaction with lattice vibrations and for this reason the life-time of exciton in tetracene strongly decreases with increasing temperature. This in turns leads to a strong dependence of the diffusion length on temperature. Thus, in order to obtain an efficient indirect pumping at a given temperature, it is necessary to use a tetracene layer thickness L smaller or equal to the diffusion length L_D at this temperature. Otherwise, the energy transfer from tetracene to the II–VI quantum well will be suppressed because due to fission only triplet excitons and not singlet excitons will be able to reach the barrier of the quantum well. These remarks tell us that for a given tetracene thickness L the indirect pumping via singlet excitons can be efficient only in a restricted temperature interval up to a critical temperature T_c which decreases with increasing L.

For our quantitative estimations, we make use of an analytical expression for the energy transfer efficiency $\mathcal{E}$ (the ratio between the number of transferred energy quanta and the total number of incident photons) from our recent paper (Eq. (4) in Ref. [3], with $z_0 = 0$) which is very accurate for most cases of practical interest, including the one of tetracene as well:

$$\mathcal{E} = \frac{\alpha^2 L_D^2}{(\alpha^2 L_D^2 - 1)\cosh(L/L_D)} \times$$
$$\times \left\{1 - e^{-\alpha L}[\cosh(L/L_D) + (\alpha L_D)^{-1}\sinh(L/L_D)]\right\}. \quad (1)$$

We recall that L is the thickness of the tetracene layer, α – the tetracene absorption coefficient, and L_D – its diffusion length, the only quantity here which crucially depends on temperature (see Fig. 2). While this result appears to be fairly simple, its validity hinges on a rather technical scrutiny accounting for the specific dependence on distance of the energy transfer [3].

The results obtained for the energy transfer efficiency $\mathcal{E}$, duly taking the temperature dependence of L_D into account, are presented in Fig. 3 for different

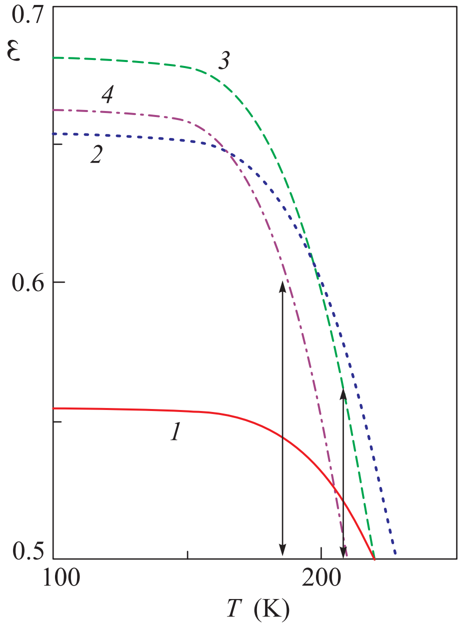

Fig. 3. (Color online) Temperature dependence of energy transfer efficiency for different tetracen layer thicknesses: $L = 200$ Å for the red continuous line (case *1*, $T_c = 256$ K), $L = 300$ Å for the blue dotted line (case *2*, $T_c = 226$ K), $L = 400$ Å for the green dashed line (case *3*, $T_c = 206$ K), and $L = 500$ Å for the purple dash-dotted line (case *4*, $T_c = 184$ K)

thicknesses of the tetracene thin layer ($L = 200$ Å for case *1*, $L = 300$ Å for case *2*, $L = 400$ Å for case *3*, and $L = 500$ Å for case *4*). Vertical lines with arrows mark the critical temperature T_c at which $L_D(T_c) = L$, beyond which the process of fission becomes so efficient that mainly triplet excitons rather than singlet excitons can diffuse to the barrier of the II–VI quantum well. The lifetime of triplets in tetracene is $0.6 \pm 0.1\,\mu$s, their diffusion length is $L_D = 1000 \pm 100$ Å and their diffusion constant $D = (1.6 \pm 0.8) \cdot 10^{-4}\,\text{cm}^2\,\text{s}^{-1}$ [7]. Of course, while triplets do not have enough energy to contribute to the indirect pumping of the II–VI quantum well here considered, they may take part to other processes, including charge generation.

For a given tetracene thickness, a temperature change from $T < T_c$ to $T > T_c$, the time scale of which will be most likely limited by the tiny heat capacity of the sample, can quench the indirect pumping of the quantum well because thermally activated fission of singlets occurs transforming them into triplets. As expected, the critical temperature goes down to low temperatures when the thickness of the tetracene layer is increased; in particular, we find $T_c = 256$ K for case *1*, $T_c = 226$ K for case *2*, $T_c = 206$ K for case *3*, and $T_c = 184$ K for case *4*. In fact, larger layer thicknesses require longer diffusion lengths for the energy transfer to be efficient and, correspondingly (see Fig. 2), lower temperatures as shown on Fig. 3.

It remains to be explained why at low temperatures the order in which $\mathcal{E}$ is increasing corresponds to the sequence *1–2–4–3* rather than *1–2–3–4*, i.e. simply according to the layer thickness ordering. This inversion can be understood taking into account the relation between the layer thickness L and the value of the absorption length $1/\alpha$ of resonant light in the tetracene crystalline layer ($\alpha \simeq 2 \cdot 10^5\,\text{cm}^{-1}$). In the cases *1*, *2*, and *3* the absorption length is larger than the layer thickness and the beneficial effect of increasing absorption dominates the dependence of $\mathcal{E}$ on L. It is however clear that for layers thicker than the absorption length the energy transfer efficiency will decrease when the thickness of the tetracene layer increases as the singlets have to diffuse over a longer distance while the absorption has saturated. In case *4*, with a thickness comparable to the absorption length, $\mathcal{E}$ is diffusion limited and for this reason is smaller than in the other cases.

Finally, it is to be noticed that in cases *2*, *3*, and *4* the efficiency of energy transfer is larger than for the case of anthracene ($\mathcal{E} = 60\,\%$) we considered in Ref. [3].

Concluding remarks. We considered a hybrid heterostructure made of an inorganic quantum well in close proximity with a crystalline tetracene overlayer to indirectly pump the optical nonlinearities of the two-dimensional Wannier excitons. The energy of the lowest singlet exciton in tetracene is almost twice the one of the lowest triplet exciton and singlet exciton fission into two triplets at high temperature can be efficient. Thus, tetracene can be useful for indirect pumping in an hybrid nanostructure only when singlet excitons are stable and able to deliver energy to the inorganic quantum well. The fission of singlet excitons in tetracene is thermally activated and the temperature at which the process of fission quenches the energy transfer strongly depends on the thickness of the tetracene layer. We showed that due to this property of tetracene the indirect pumping of the inorganic quantum well in the hybrid structure here considered can be turned on and off depending on temperature. This behaviour will similarly affect the functional properties of other hybrid nanostructure based on tetracene.

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