

Nonradiative exciton energy transfer in hybrid organic-inorganic heterostructures

S. Chanyawadee,¹ P. G. Lagoudakis,^{1,*} R. T. Harley,¹ D. G. Lidzey,² and M. Henini³

¹*School of Physics and Astronomy, University of Southampton, Southampton SO17 1BJ, United Kingdom*

²*Department of Physics and Astronomy, The University of Sheffield, Sheffield S3 7RH, United Kingdom*

³*School of Physics and Astronomy, University of Nottingham, Nottingham NG7 2RD, United Kingdom*

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Nonradiative energy transfer from a GaAs quantum well to a thin overlayer of an infrared organic semiconductor dye is unambiguously demonstrated. The dynamics of exciton transfer are studied in the time domain by using pump-probe spectroscopy at the donor site and fluorescence spectroscopy at the acceptor site. The effect is observed as simultaneous increase in the population decay rate at the donor and of the rise time of optical emission at the acceptor sites. The hybrid configuration under investigation provides an alternative nonradiative, noncontact pumping route to electrical carrier injection that overcomes the losses imposed by the associated low carrier mobility of organic emitters.

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The brightness and flexibility of organic semiconductors have rendered them as promising new materials for the optoelectronic industry^{1,2} with full color displays and flexible screens being a few of the upcoming applications. Although organic emitters are, in general, brighter than their inorganic counterparts, the unresolved issue of low carrier mobility in organic compounds poses limitations on the total efficiency of these devices^{3,4} and is partly responsible for the unattainable of an electrically pumped organic laser. A route to circumvent altogether issues associated with low carrier mobility in organic emitters is to engineer devices that utilize alternative pumping schemes to electrical injection and transport while still benefiting from the brightness of the organic dyes. By tailoring the optoelectronic properties of a hybrid organic-inorganic material system, carriers could be injected and transported into the inorganic part and be subsequently directly transferred in a noncontact way to the organic emitter. Rapid and efficient energy transfer can occur either by coherently coupling the inorganic and organic semiconductors in the strong coupling regime⁵⁻⁷ or by nonradiative energy transfer from an inorganic semiconductor slab to an organic overlayer.^{8,9} In the latter process, no real photons are involved and the efficiency of the transfer process between donor and acceptor sites, as first studied by Förster,¹⁰ can exceed that of radiative energy transfer routinely used in phosphor light emitting devices.¹¹ The first experimental evidence of the above mechanism was observed in hybrid structures between the Wannier excitons in wide band gap semiconductor quantum wells (donors) and colloidal semiconductor quantum dots^{12,13} (acceptors) or the Frenkel excitons in organic fluorophores.¹⁴⁻¹⁶

Time-resolved studies in hybrid quantum well heterostructures have demonstrated the effect of an extra decay channel in the quantum well emission (donor).¹²⁻¹⁴ However, this alone cannot be taken as evidence of energy transfer to the acceptor sites because the deposition of an overlayer of organic dye molecules, fluorophores, or colloidal quantum dots on the quantum well barrier separating donor and acceptor sites could lead to modification of its surface states, which would itself modify the decay dynamics. Any changes in the photoluminescence decay of a quantum well in a hybrid structure can only be conclusively attributed to nonradi-

ative energy transfer to the acceptor site if the effect of energy transfer is also directly observed in the emission properties of the acceptor.¹⁵

In this Brief Report, we demonstrate nonradiative energy transfer between a single GaAs quantum well donor and an acceptor of an organic dye both at the donor's and acceptor's sites. The dynamics of exciton transfer are studied in the time domain by using pump-probe reflection spectroscopy at the donor site and time-resolved fluorescence decay measurements at the acceptor site. Furthermore, we investigate the dependence of the energy transfer efficiency on the spectral overlap between donor and acceptor by varying the width of the single quantum well donor. The precise growth of the GaAs heterostructures allows us to controllably modify the spectral overlap between donor and acceptor in the hybrid structure while accurately controlling the distance between quantum well excitons and organic molecules.

The organic-inorganic hybrid structures consist of a GaAs/AlGaAs single quantum well (donor) and an organic dye (U3) overlayer (acceptor), as shown in Fig. 1(a). Dye U3 (3-[(2Z)-5-chloro-2-[[[(3E)-3-[[5-chloro-3-(3-triethylammonium-sulfonatopropyl)-1, 3-benzothiazol-3-ium-2-yl]methylene}-2,5,5-trimethylcyclohex-1-en-1-yl]methylene]-1,3-benzothiazol-3(2H)-yl] propane-1-sulfonate) was synthesized by interaction of two equivalents of 3-(5-chloro-2-methyl-1,3-benzothiazolium-3-yl) propane-1-triethylammonium-sulfonate with one equivalent of 1, 3-diethoxy-2,5,5-trimethyl-1,3-cyclohexadiene at 145–150 °C in the presence of triethylamine. The total chemical formula of the dye U3 is C₃₇H₄₉Cl₂N₃O₆S₄ with a molecular weight of 831.6 g/mol. The organic material is dissolved in methanol and spin coated on the quantum well to form a uniform film with a nominal thickness of 12 nm [Fig. 1(b)]. By varying the concentration of the initial solution of the dye, we control the thickness of the organic overlayer with ±15 nm accuracy [inset of Fig. 1(b)]. The infrared emitting dye that we have used¹⁷ when dissolved in methanol and spin coated on a glass substrate has an absorption spectrum, as shown in Fig. 1(c) (dashed-dotted curve, red online). The single GaAs/Al_{0.35}Ga_{0.65}As quantum well structures are grown by molecular beam epitaxy on (100) GaAs substrates with a 500 nm GaAs buffer layer. In sample A, the quantum

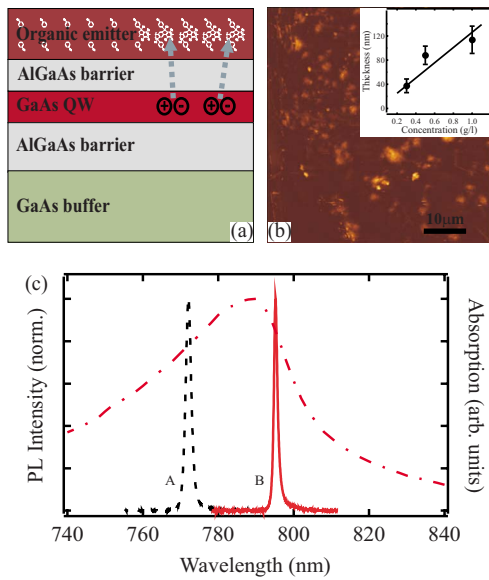


FIG. 1. (Color online) (a) Schematic diagram of organic-inorganic hybrid structures. Organic dye is deposited on 4.0 (sample A) and 6.5 nm thick (sample B) quantum wells. (b) Atomic force microscopy image of organic dye layer deposited on a glass substrate. Inset: thickness of the organic film vs concentration of organic dye. (c) Spectral overlaps between the emission of sample A (dashed curve) and of sample B (solid curve, red online) at 25 K and the absorption of organic dye (dashed-dotted curve, red online).

well width is 4 nm, while in sample B, the width is 6.5 nm. For both structures, the width of the inner barrier is 20 nm, with the top barrier (which also controls the separation between quantum well excitons and organic molecules) being 7.5 nm. The photoluminescence spectrum of the two single quantum well structures at 25 K is shown in Fig. 1(c). Sample A has a photoluminescence peak at 772 nm (dashed curve), while sample B has a photoluminescence peak at 795 nm (solid curve, red online). Thus, by varying the thickness of the single quantum well, the spectral overlap between the photoluminescence of the quantum well and the absorption of the organic overlayer can be controllably tuned.

The broad fluorescence spectrum of the organic emitter and its overlap with the photoluminescence spectrum of the quantum well make it impossible to study both donor and acceptor using photoluminescence alone. Therefore, we use pump-probe reflectivity measurements to study the transfer dynamics from the quantum wells to the organic overlayer combined with spectrally resolved time-correlated single photon counting measurements of the fluorescence from the organic dye. Pump-probe reflectivity measurements have allowed for characterization of the transient dynamics of excitons in the quantum wells while being insensitive to the presence of a thin organic overlayer. A schematic of the pump-probe setup is shown in Fig. 2(a). A tunable mode-locked Ti:sapphire oscillator with 76 MHz repetition rate and ~ 2 ps pulse width (spectral width of 0.8 meV) is used to excite the quantum well resonantly with the $n=1$ heavy hole excitonic absorption. The pump-induced change of the reflected probe intensity (ΔR) is measured by scanning the time delay between pump and probe pulses. Small pump-induced changes

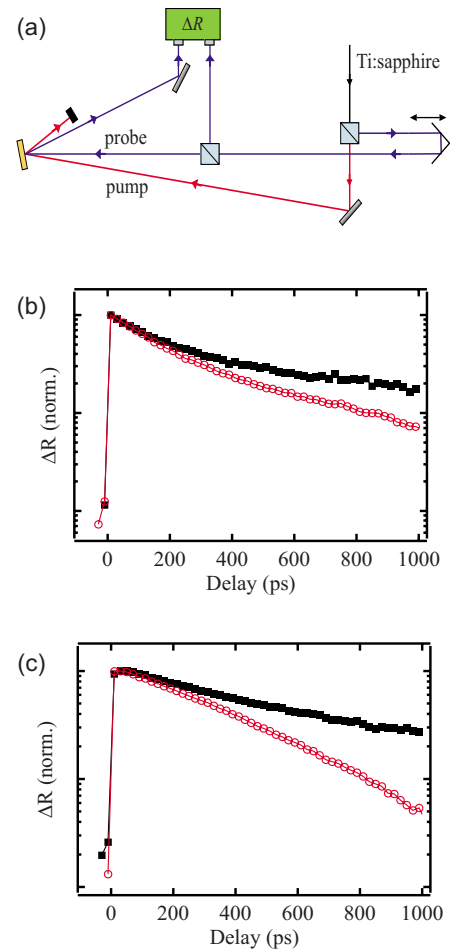


FIG. 2. (Color online) (a) A schematic of the pump-probe setup. Normalized population decays of the bare quantum wells (solid squares) and the quantum wells in the hybrid structures (open circles, red online) for (b) sample A and (c) sample B.

of the reflected probe beam are measured by using the balanced photodiodes and a lock-in detection scheme in a cold finger cryostat at 7 ± 2 K.¹⁸

Figures 2(b) and 2(c) show the population decay (ΔR) of the quantum wells only (solid squares) and the population decay of quantum wells in the presence of the organic overlayer (open circles, red online). The excitation wavelengths are 768 and 792 nm for samples A and B, respectively. The faster depopulation in the hybrid organic-inorganic structure demonstrates that the presence of the organic layer results in an additional decay channel. The decay time for sample A decreases from 326 to 235 ps, whereas that for sample B decreases from 642 to 389 ps, and the additional decay rate in the hybrid configuration, k_{ET} , can be derived from the photoluminescence decay rate of the hybrid structure ($k_H = \tau_H^{-1}$) and of the bare QW ($k_{QW} = \tau_{QW}^{-1}$) from $k_{ET} = k_H - k_{QW}$.

Alone, this result does not demonstrate that the onset of the extra decay channel in the quantum well emission is due to energy transfer to the organic overlayer. To do this, we directly compare the time evolution of the fluorescence of the organic dyes in the hybrid structures and on glass substrates where no energy transfer occurs by using spectrally filtered, time-correlated single photon counting. Figure 3

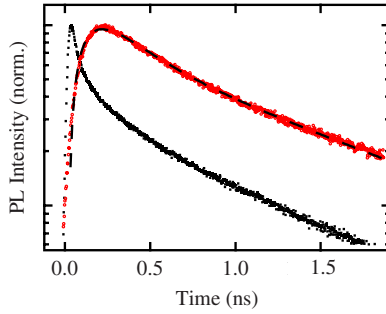


FIG. 3. (Color online) Photoluminescence decays of organic dye deposited on a glass substrate (solid squares) and on a single quantum well (sample A, open circles, red online). The dashed curve is the fit using Eq. (3).

compares the fluorescence on a glass substrate (solid squares) with that on sample A (solid circles, red online). Here, both structures are excited at 745 nm and spectral filters are used to select the fluorescence of the organic dyes only while the samples are held in a cold finger cryostat at 25 K. Evidently, the emission rise time from the hybrid structure is considerably slower, which clearly indicates the energy transfer from the quantum well excitons to the organic dye.

Following the direct observation of the transfer to the organic overlayer, the extra rate, k_{ET} , estimated from the pump-probe measurements on the quantum wells can be confidently assigned to nonradiative energy transfer. The efficiency of the process is derived from $\eta = k_{ET}/(k_{ET} + k_{QW})$, which for samples A and B is $\eta_A = 0.23$ and $\eta_B = 0.39$, respectively. Theoretically, the energy transfer rate linearly scales with the spectral overlap between donor and acceptor.^{10,19} We therefore expect here the ratio of the transfer rate of the two hybrid structures, $k_A/k_B = 1.18 \pm 0.21$, to be equal to the ratio of the corresponding spectral overlaps of the two quantum wells (samples A and B) with the organic dye absorption spectrum. From the data of Fig. 1(c), we obtain for this ratio $\Omega_A/\Omega_B = 1.27$ which is indeed reasonably close to the ratio of transfer rates. This agreement further confirms the nature of the process and the validity of the pump-probe technique to characterize nonradiative energy transfer in hybrid structures.

To quantitatively correlate the results of nonradiative energy transfer at the donor and acceptor sites, we use a simple kinetic model to describe exciton dynamics in the quantum well and the organic layer. The transient fluorescence of the organic dye is approximated by a slow and a fast decaying population to fit the biexponential character of the measured fluorescence decay. The two distinctive decay channels of the organic dye can be attributed to the decay of the Frenkel excitons from uncoupled monomers and of aggregates of the dye molecule. Based on these approximations, we use the following set of equations to model the hybrid structure under study:

$$\frac{dN_{QW}}{dt} = -k_{QW}N_{QW} - k_{ET}N_{QW}, \quad (1)$$

$$\frac{dN_{OGi}}{dt} = -k_{OGi}N_{OGi} + C_i k_{ET}N_{QW}, \quad (2)$$

where $i=1,2$, N_{QW} and N_{OGi} are exciton populations in the quantum well and the organic overlayer, respectively, $k_{OG1} = 1 \times 10^{10} \text{ s}^{-1}$ and $k_{OG2} = 8.3 \times 10^8 \text{ s}^{-1}$ are the fluorescence decay rates of the bare organic layer as derived from the fast and slow components of its almost biexponential decay (Fig. 3, solid squares), and $C_{1,2}$ are constants with $\sum_i C_i = 1$. By neglecting the direct laser-induced exciton population of the organic dye due to the narrow bandwidth of the excitation pulse and assuming an initial population for the resonantly excited quantum well, the analytical solution of the above set of equations for the fluorescence decay of the organic dye is

$$I(t) = \sum_i \frac{C_i N_{QW}(t=0) k_{ET}}{k_{OGi} - k_{QW} - k_{ET}} (e^{-(k_{QW} + k_{ET})t} - e^{-k_{OGi}t}). \quad (3)$$

The dashed curve in Fig. 3 is a fit of the measured fluorescence decay (solid circles, red online) in the hybrid configuration using Eq. (3) (with $C_1/C_2 = 4$ expressing the contribution of the fast and slow components of the organic dye on the fluorescence decay). Considering that the photoluminescence decay rate k_{QW} , the nonradiative energy transfer rate k_{ET} , and the fluorescence decay rates k_{OG1} , k_{OG2} are not free parameters but are taken from the pump-probe measurements and the fluorescence decay of the organic dye on glass, respectively, there is a very good agreement between this simple model and the experimental observation.

In the rapidly developing field of hybrid optoelectronics, where organic and inorganic semiconductors are merged in novel configurations that exploit the advantages of the individual compounds, nonradiative energy transfer is shown to play an important role. It allows for tunneling of energy in a noncontact, nonradiative way that overcomes limitation imposed by the low carrier mobility in organic semiconductors. The measurements we have described provide conclusive evidence of nonradiative energy transfer from a semiconductor quantum well to an overlayer of organic dye in the near-infrared regime by resolving the processes both at the donor and acceptor sites, thereby excluding other nonradiative mechanisms that could influence the photoluminescence properties of the quantum well only. Furthermore, by appropriate engineering of the semiconductor materials, we observe high nonradiative energy transfer efficiencies (23% sample A and 39% sample B) that indicate the applicability of the process in real-world hybrid optoelectronic devices. Future work will address the issue of electrically generated emission from such devices and the realization of a hybrid organic-inorganic injection laser diode.

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*Corresponding author; pavlos.lagoudakis@soton.ac.uk

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