Ultrafast polariton relaxation dynamics in an organic semiconductor microcavity

T. Virgili,[1,*] D. Coles,[2] A. M. Adawi,[2,‡] C. Clark,[3] P. Michetti,[4] S. K. Rajendran,[1] D. Brida,[1] D. Polli,[1] G. Cerullo,[1] and D. G. Lidzey[2,†]

[1]*IFN, CNR Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo Da Vinci 32, 20133 Milano, Italy*

[2]*Department of Physics and Astronomy, University of Sheffield, Hicks Building, Hounsfield Road, Sheffield S3 7RH, United Kingdom*

[3]*Helia Photonics Ltd. Rosebank Park, Livingston, West Lothian EH54 7EJ, United Kingdom*

[4]*Institute of Theoretical Physics and Astrophysics, University of Würzburg, D-97074 Würzburg, Germany*

(Received 4 May 2011; published 20 June 2011)

We study an organic semiconductor microcavity operating in the strong-coupling regime using fs pump-probe spectroscopy. By probing the induced absorption associated with the one-exciton to two-exciton transition, we are able to characterize the time-dependent population densities of states in the upper- and lower-polariton branches following impulsive excitation. We model the time-dependent polariton dynamics and provide direct evidence of a scattering process that returns upper-branch cavity polaritons to states in the exciton reservoir having a rate of $(150\ \text{fs})^{-1}$. A slower process similarly populates lower-branch polaritons by return scattering from the exciton reservoir.

DOI: 10.1103/PhysRevB.83.245309 PACS number(s): 71.36.+c, 42.65.−k, 78.47.D−

I. INTRODUCTION

A microcavity is a structure in which two mirrors are placed in close proximity and are separated by a thin film of an active semiconductor material. Within the strong coupling regime, the confined optical modes of the cavity undergo a coupling with the semiconductor excitons resulting in the formation of cavity-polariton states. Such cavities are characterized by at least two polariton branches, the upper polariton (UP) and the lower polariton (LP), that are split at the point of exciton-photon resonance by the Rabi-splitting energy.[1] A number of organic semiconducting materials have been shown to undergo strong coupling in a microcavity.[2–12] Strong coupling is of significant theoretical and practical importance, as work on inorganic semiconductor-based systems has shown that the polariton states formed can undergo scattering to form a nonequilibrium condensate that is trapped in momentum space at the bottom of the LP branch. Such condensates can have long-range spatial and temporal coherence,[13] display collective dynamics characteristic of superfluidity,[14] and undergo lasing with a low threshold.[15,16] Lasing effects have very recently been observed in a strong-coupled cavity containing a single crystal of the molecular dye anthracene.[17]

The optical properties of organic-based microcavities are in most cases dominated by the effects of energetic and positional disorder. This, it has been argued,[18–23] results in a system in which the majority of states (>0.99) are stationary and uncoupled to light, forming a so-called "exciton reservoir." Indeed, polariton states are only formed having a relatively narrow range of in-plane momenta centered on the point where exciton and photon undergo anticrossing. Such polariton states are delocalized and characterized by well-defined wave vectors and coexist with localized excitons within the cavity.[22] This coexistence of delocalized polaritons and localized excitons has a profound effect on the relaxation dynamics of the system; it has been proposed that uncoupled excitons created in the exciton reservoir can only scatter into the exciton component of a polariton state by first losing an appropriate amount of energy to a localized vibrational mode.[23] Similarly UPs are thought to be able to scatter nonradiatively into a vibrationally excited state in the exciton reservoir.[18,19] Calculations that consider exciton scattering with a continuum of vibrational modes have been shown to provide a good qualitative description of cavity emission.[24]

At present, relatively little direct experimental validation has been presented for the interplay between exciton-polaritons and reservoir excitons in an organic microcavity. We have previously shown[25,26] that the population of UP states around resonance is dependent on the energetic separation between the UP branch (described by a Maxwell-Boltzmann distribution) and the super-radiant states that exist at the bottom of the exciton reservoir that approximately coincide with the peak absorption energy of the J-aggregate thin film. However this simply provides indirect evidence of the exchange of population between the exciton reservoir and UP states. In this paper we provide direct evidence of the transfer of population between the exciton reservoir and upper- and lower-branch polariton states using fs pump-probe spectroscopy. We show that UP states are able to scatter to the exciton reservoir with a rate of $(150\ \text{fs})^{-1}$. We show that our spectroscopy measurements are in good agreement with theoretical models of relaxation processes within strongly coupled organic-semiconductor microcavities, confirming our growing understanding of such photonic systems.[18,19,22]

II. EXPERIMENTAL METHODS

The microcavities studied are based on a double dielectric-mirror structure containing a thin film of a J-aggregated cyanine dye (TDBC) (5,6-dichloro-2-[[5,6-dichloro-1-ethyl-3-(4-sulphobutyl)benzimidazol-2-ylidene]propenyl]-1-ethyl-3-(4-sulphobutyl) benzimidazolium hydroxide, inner salt, sodium salt) suspended in a polyvinyl alcohol matrix as shown schematically in Fig. 1(a). Here the bottom distributed Bragg reflector (DBR) is composed of 11 $\lambda/4$ pairs of TiO_2 and SiO_2. The J-aggregate containing thin organic film was deposited onto this mirror by spin coating from solution. Onto this, a second DBR mirror was deposited by physical-vapor

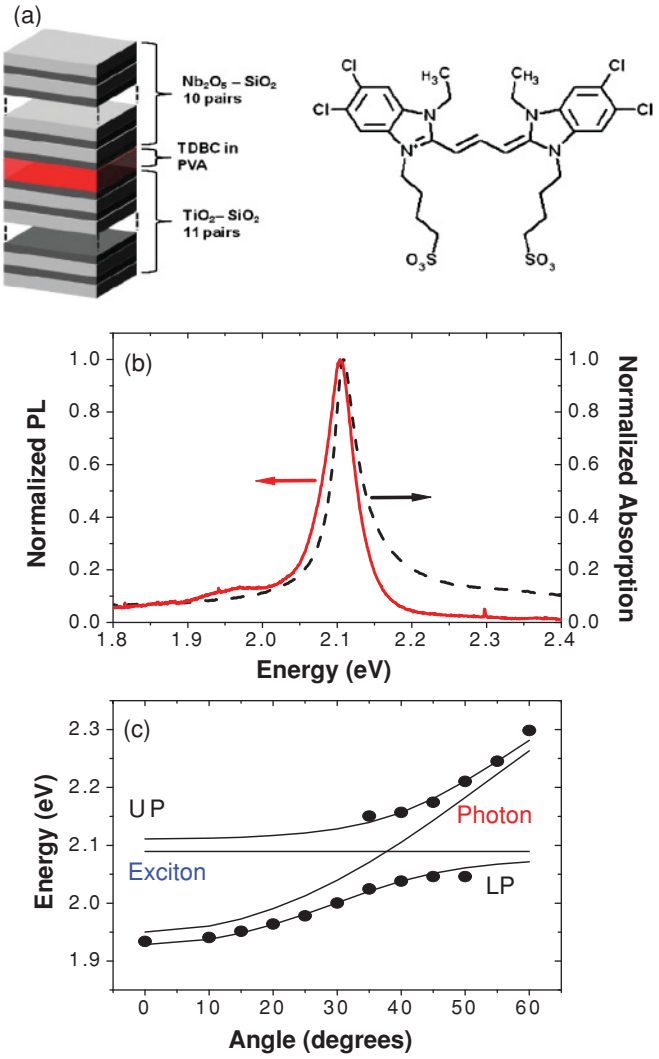

FIG. 1. (Color online) (a) A schematic of the microcavity studied together with the chemical structure of the TDBC dye. (b) The absorption (dash line) and photoluminescence (solid line) of a control thin film of TDBC. (c) The dispersion of the cavity modes as determined from white-light reflectivity measurements. The best fit to the measured data points using a two-level model is shown using a solid line. The exciton-photon resonance is found at $\theta = 38^\circ$ with a Rabi-splitting energy of 120 meV.

deposition and was composed of 10 $\lambda/4$ layers of SiO_2 and Nb_2O_5.

The J-aggregated cyanine dye has an optical transition at 2.10 eV with a line width of 35 meV, the so-called "J-band" [see Fig. 1(b)]. Emission is similarly narrow, and it is Stokes shifted by 4 meV. A weaker low-energy emission feature at 1.975 eV most likely corresponds to unaggregated TDBC molecules and molecular dimers. Figure 1(c) shows the anticrossing behavior between the exciton and the photon modes. At exciton-photon resonance ($\theta = 38^\circ$) a doublet of cavity-polariton states are detected having a Rabi-splitting energy of 120 meV.

We have performed ultrafast pump-probe spectroscopy on both the bare TDBC J-aggregate dye and the strongly coupled microcavity. The pulses were derived from two noncollinear optical parametric amplifiers (OPAs) using β-barium borate crystals.[27] Each OPA was pumped by the second harmonic of a Ti:sapphire laser, seeded by a white-light continuum, and compressed by a chirped mirror pair. The degenerate pump and probe pulses (delivered at 1 kHz) were spectrally broad (having a bandwidth of ~380 meV), peaked at 2.13 eV, and had a temporal duration of 15 fs. In our setup the pump and probe pulses had a parallel polarization and were almost collinear. The pump and probe beams were spatially overlapped on the sample and were focused to an ≈80-μm-diameter spot on the sample surface resulting in an excitation energy density of ~6 mJ cm^{-2}. The transmitted probe pulse was then detected via a computer-controlled, optical multichannel analyzer. This setup allows recording of two-dimensional differential transmission ($\Delta T/T$) maps as a function of probe frequency and delay. The spectral resolution of the system was measured to be ≈4 nm. The cavity was excited at 45°, and thus the broadband pump pulse was resonant with both UP and LP states.

Fluorescence-decay lifetime has also been measured using 150-fs pulses at 440 nm (delivered at 80 MHz) with a power density of 80 mW cm^{-2} from a frequency-doubled Ti:sapphire laser and a streak camera to detect the decay transient. All measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

Figure 2(a) shows a $\Delta T/T$ spectrum recorded from a control film of TDBC J-aggregates at 200 fs pump-probe delay. As it can be seen, the spectrum divides into a region of induced transparency, corresponding to ground-state photobleaching (PB) and one of photoinduced absorption (PA). Despite the fast component present in the PA kinetic, possibly attributable to intramolecular vibrational relaxation within the photoexcited S_1 state,[28] both features decay with similar dynamics as shown in Fig. 2(b), indicating that the PA results from a transition from the one-exciton state to a two-exciton state.[29–31] We have also measured the fluorescence-decay lifetime of a control thin film of TDBC (not shown here). We evidence a largely mono-exponential decay process with a lifetime of 25 ps time constant (for a power excitation density of 80 mW cm^{-2}) that appears strongly dependent on the intensity of the excitation laser. The faster excited state decay observed in the pump probe is ascribed to rapid exciton-exciton annihilation that rapidly depopulates multiple excitations on an aggregate.[32]

We now turn our attention to measurements on the strongly coupled microcavity. The laser pulses (pump and probe) are placed at 45° with respect to the normal direction to the cavity. Figure 3(a) shows the continuous wave transmission of the probe through the microcavity at this angle. We observe strong transmission through two optical modes at 2.05 and 2.18 eV, corresponding to the two cavity-polariton states as confirmed by the dispersion plot. In Fig. 3(b) we plot the $\Delta T/T$ spectrum of the microcavity recorded at 100 fs pump-probe delay. This spectrum consists of three identifiable PA bands that are centred at 2.04, 2.12, and 2.17 eV and a strong PB feature at ~2.09 eV. The features at 2.09 and 2.12 eV coincide with similar features identified in the control TDBC film. It appears, therefore, that at 100 fs a population of uncoupled excitons exist within the cavity. As we argue below, these states are not

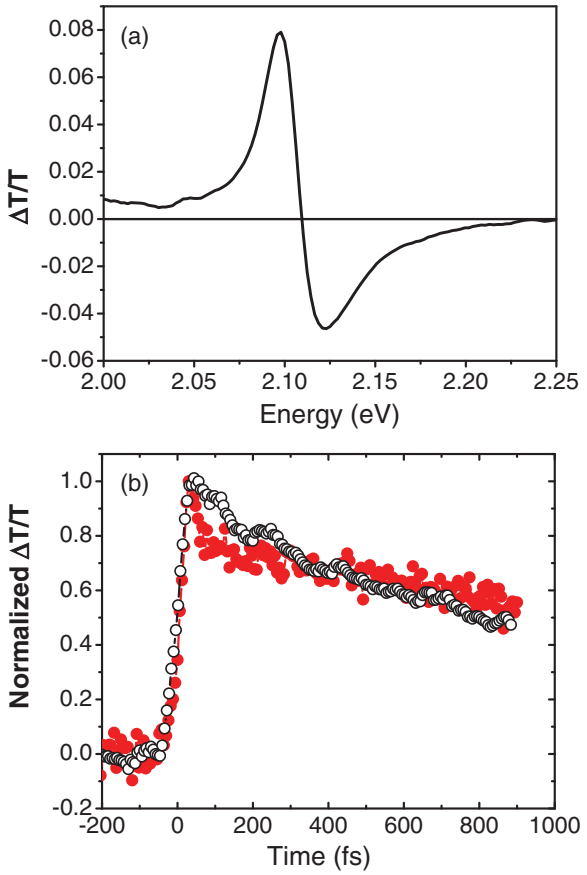

FIG. 2. (Color online) (a) A pump-probe spectrum recorded from a control TDBC thin film recorded at 200 fs after the laser pump. (b) The decay of the transient absorption (red line, closed circles) and transient photo bleach (black line, open circles).

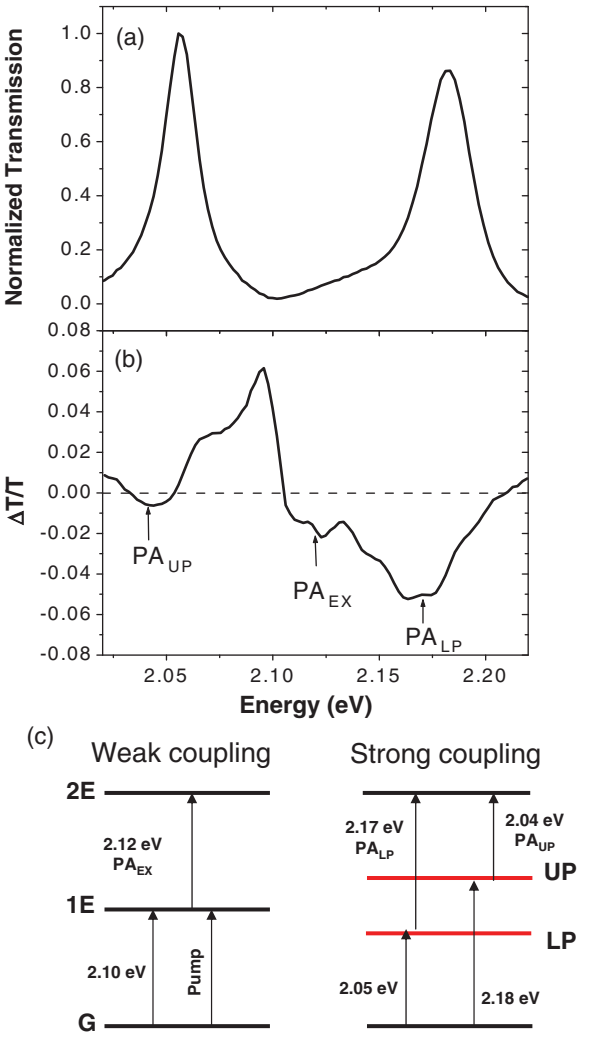

FIG. 3. (Color online) (a) The c.w. transmission of the probe through the cavity recorded at 45°. (b) The pump-probe spectrum recorded from the cavity at 100 fs after the laser pump. The pump and probe pulses are placed at 45° with respect to the normal direction to the cavity. (c) An energy-level schematic of the weak-coupled one- (1E) and two-exciton (2E) states (left), and a strongly coupled one-exciton state (right). The energy corresponding to the induced absorption transition between the UP and LP branches and the 2E level is indicated.

directly created by the pump laser but are generated following the nonradiative scattering of upper-branch polaritons toward the exciton reservoir.

We can understand the origin of the other features present in the $\Delta T/T$ spectrum as illustrated schematically in Fig. 3(c). Here, we plot an energy-level scheme for the one-exciton state when either weakly coupled or strongly coupled to the cavity photon. When strongly coupled, the one-exciton state splits forming two polariton states. Optical transitions are now possible from the one-exciton component of each polariton state to the two-exciton state as indicated. We therefore identify the PAs observed around 2.17 (2.04) eV as corresponding to a transition between the one-exciton component of the LP (UP) state to the higher lying two-exciton state and label them in Fig. 3(b), (c) as PA_{LP} and PA_{UP}, respectively. In the same figures we also label the one-exciton to two-exciton transition as PA_{EX}. We can use the magnitude of the transient absorption recorded close to these two energies as a time-dependent probe of the relative population of the LP and UP branches. Note that we assume that the one-exciton to two-exciton transition is not itself dressed by the cavity-photon mode. We can test this assumption as follows. If a thin film of TDBC having a transmission of $I/I_0 = 0.20$ (determined at the peak of the absorption of the J-aggregate) is placed in a microcavity, we find that the structure has a Rabi-splitting energy of $\hbar\Omega_{\text{Rabi}} = 145$ meV. However as shown in Fig. 2(a), the pump pulse causes a change in attenuation in the control film of 5% (i.e., $I/I_0 = 0.95$). Using the fact that $\hbar\Omega_{\text{Rabi}} \approx \sqrt{\alpha L}$ (where α is the attenuation coefficient and L is film thickness),[33] it is straightforward to show that the Rabi-splitting associated with the one-exciton to two-exciton transition would be 25 meV under the pumping conditions used here; a value coincident with the measured line width of the cavity-polariton states at resonance. However this value represents an upper limit for such an interaction, as the one-exciton population generated inside the cavity will be substantially smaller than this because of the attenuation of the laser pulse resulting from the relatively high reflectivity of the dielectric mirror. We thus anticipate (at least at short time scales) that the one-exciton to two-exciton transition is uncoupled to the light field within the cavity.

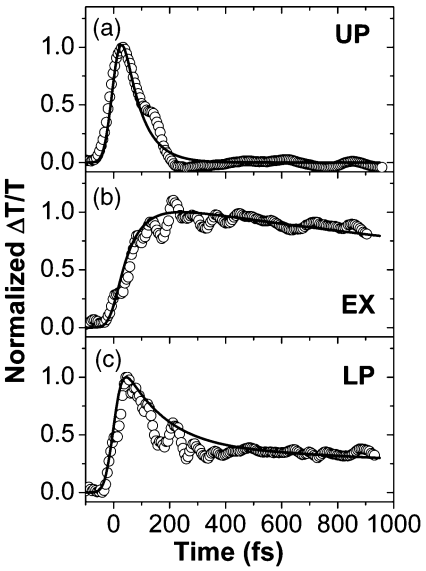

FIG. 4. (a), (b), and (c) The transient absorption recorded at 2.03, 2.13, and 2.17 eV (primarily corresponding to the UP, exciton-reservoir, and LP branch, respectively). In each case, a best fit to the measured data points is shown using a solid line.

In Fig. 4(a)–(c) we plot the kinetics of the PA transitions recorded at 2.03, 2.13, and 2.17 eV. These are energies approximately coincident with the peak of the PA of the one-exciton population in the upper branch, the exciton reservoir, and the lower branch, respectively. Here, measured data are plotted using filled circles with the solid lines being the results of a best fit to a kinetic model that we describe below. It can be seen in Fig. 4(a) that the population of UP is created very rapidly as the 15-fs pump pulse is absorbed in a few tens of fs (corresponding to a few round trips in the cavity). The UP population then undergoes a rapid decay, reaching $\Delta T/T \approx 0$ after 250 fs. We propose that this process is the combination of radiative decay and ultrafast relaxation that populates excited states within the exciton reservoir.

A qualitatively different behaviour is observed when we probe the population of the exciton reservoir [Fig. 4(b)]. Here, the pump pulse does not instantaneously create a significant population of reservoir states; however, such states undergo a grow-in with $\Delta T/T$ reaching a maximum value at ∼250 fs. After this time, the exciton population decays with a time constant that is longer than 5 ps. The grow-in of the reservoir population suggests that such excitons are mainly created as UP population decays back to the reservoir, suggesting that the exciton reservoir is only weakly coupled to the external light field. This observation is consistent with the fact that, at exciton-photon resonance, the peak absorption energy of the TDBC J-aggregates (at 2.10 eV) coincides with a transmission minimum [see Fig. 3(a)]. We note that the decay of states of the exciton-reservoir population has a time constant that is longer than one-exciton decay transient recorded via pump probe from the control film. This is consistent with the fact that, in a high-quality microcavity, the absorbed fraction of incident light is smaller than for a bare film, thus resulting in a lower exciton density. In Fig. 4(c) we plot the decay of the population in the LP. Here, the impulsive pump rapidly generates polaritons; however, in contrast to the upper-branch states, the decay of population occurs with time constants of ∼150 fs and tens of ps. We associate the fast-time constant to radiative decay. The slow-time constant is consistent with the decay dynamics of the exciton reservoir indicating that lower-branch states are continually replenished from the slowly decaying reservoir population, thus reaching equilibrium.

It can be seen that there is a high-frequency modulation of the population of the polariton branches and the exciton reservoir that persists for around 500 fs after the initial excitation. This effect, we believe, results from the excitation of a range of different intramolecular phonons that are generated as a result of nonradiative transitions from the UP branch to the exciton reservoir and from reservoir excitons to polariton states on the LP branch.[23]

We have modelled the decay dynamics of both polariton branches and the exciton reservoir using the following coupled rate equations:

$$\dot{N}_u(t) = G_u(t) - N_u(t)\left[\alpha_u\Gamma_c + \Gamma^s_{u\to x}\right] \quad (1)$$

$$\dot{N}_x(t) = G_x(t) + N_u(t)\Gamma^s_{u\to x} - N_x(t)\Gamma^s_{x\to l} \quad (2)$$

$$\dot{N}_l(t) = G_l(t) + N_x(t)\Gamma^s_{x\to l} - N_l(t)\alpha_l\Gamma_c. \quad (3)$$

Here, $N(t)$ is the time-dependent number of particles, in which the subscripts u, l, and x label the UP branch, LP branch, and exciton reservoir, respectively. We assume that the pump laser prepares a population of polaritons in the upper and lower branches and a smaller number of uncoupled excitons in the reservoir. As our experiments were performed at small positive detuning ($\theta = 45^\circ$), the UP states contain a lower exciton fraction than do the LP states and are therefore not pumped as efficiently by the incident laser. We also assume that the laser generates a small number of uncoupled excitons in the exciton reservoir. We model this process using time-dependent generation terms $G_{u,l,x}(t)$ centered at $t = 0$ that are assumed to have the form of Gaussian functions having a full-width half maximum of 35 fs (a value larger than the width of the pump-probe cross correlation because of the photon-trapping effect in the cavity). The polariton population in the upper and lower branches are then able to undergo optical decay at a rate that is the product of the radiative decay rate of photons from the cavity (Γ_c) and the photon fraction of the polariton state ($\alpha_{u,l}$) that at resonance is equal to 0.5. From our two-level fit to the polariton dispersion curve, we find that $\alpha_u = 0.54$ and $\alpha_l = 0.46$ at $\theta = 45^\circ$. Both excitons and polaritons are also able to undergo scattering to another state (indicated by Γ^s). In all cases, the subscripts u, l, and x label the initial and final state involved in each decay process. It was not necessary to include a term describing the radiative decay of reservoir excitons to achieve a satisfactory description of the data. This suggests that the radiative decay of uncoupled reservoir excitons occurs over much longer time scales than the processes probed here. It was also not necessary to include any transfer of population from the exciton reservoir to the upper branch, or return of lower-branch polaritons to the reservoir. This is not unexpected, as the energy separation between the exciton reservoir and the polariton branches (>50 meV) is much larger than kT at room temperature.

To relate the PA signals measured at 2.03, 2.13, and 2.17 eV to the modelled particle densities, we assume

$PA_{2.03}(t) = \gamma_u N_u(t)$ and $PA_{2.13}(t) = \gamma_x N_x(t)$ where γ is a fitting constant proportional to the excitons and polaritons excited-state absorption cross section. It is apparent from Figs. 2(a) and 3(b), however, that there is some overlap between the LP and exciton absorption transitions at 2.17 eV. We account for this by assuming a small (22%) component of the signal recorded at 2.17 eV results from direct absorption by free excitons, i.e., $PA_{2.17}(t) = \gamma_u N_u(t) + \gamma_x 0.22 N_x(t)$.

The fits, shown in Fig. 4(a)–(c) as solid lines, display an outstanding agreement with the experimental data. Our model suggests that the radiative lifetime of cavity photons ($1/\Gamma_c$) is ~60 fs, a value in reasonable agreement with our estimate of 90 fs for cavity with a Q-factor (determined experimentally far away from resonance) of approximately 300. The rate at which UPs scatter to the exciton reservoir is $\Gamma^s_{u\to x} = (150\ \text{fs})^{-1}$; a result in good agreement with theoretical predictions.[18,19,22] We also find that reservoir excitons scatter into lower-branch polaritons with a time constant of $1/\Gamma^s_{x\to l} = 3.2$ ps. Theoretical work has suggested a range of times for this process, ranging from 9 ps[19,23] to 350 ps.[24] It is likely that the shorter scattering time we observe results from an additional (and faster) exciton decay channel—for example exciton-exciton annihilation as evidenced in the control TDBC film.

IV. CONCLUSIONS

In this paper we have studied relaxation processes in an organic-semiconductor microcavity operating in the strong coupling regime by fs-time resolution pump-probe spectroscopy. Our measurements demonstrate therefore that UP states return to the exciton reservoir at a rate of $(150\ \text{fs})^{-1}$, and that such reservoir excitons rapidly populate lower-branch polariton states, confirming predictions of population transfer to and from polariton states and the exciton reservoir.[18,19,24]

ACKNOWLEDGMENTS

We thank the UK EPSRC for funding this work via Grant EP/G062404/1 "Engineering polariton nonlinearity in organic and hybrid-semiconductor microcavities," and the European Union via FP7 ITN project Icarus (237900). P.M. thanks the DFG for financial support via Emmy Noether program (Grant No. RE 2978/1-1). We also thank Giuseppe La Rocca, David Whittaker, Andrew Ramsay, Oleksander Tsyplyatyev, and Salvatore Stagira for useful discussions during the preparation of this manuscript.

*tvirgili@polimi.it
†d.g.lidzey@sheffield.ac.uk
‡Department of Physics, University of Hull, Cottingham Road, Hull, HU6 7RX, United Kingdom.

[1] M. S. Skolnick, T. A. Fisher, and D. M. Whittaker, Semicond. Sci. Technol. **13**, 645 (1998).
[2] R. J. Holmes and S. R. Forrest, Org. Electron. **8**, 77 (2007).
[3] R. J. Holmes and S. R. Forrest, Phys. Rev. B **71**, 235203 (2005).
[4] S. Kéna-Cohen and S. R. Forrest, Phys. Rev. B **76**, 075202 (2007).
[5] D. G. Lidzey, D. D. C. Bradley, M. S. Skolnick, T. Virgili, S. Walker, and D. M. Whittaker, Nature **395**, 53 (1998).
[6] J. R. Tischler, M. S. Bradley, Q. Zhang, T. Atay, A. Nurmikko, and V. Bulovic, Org. Electron. **8**, 94 (2007).
[7] C. E. Finlayson, G. Vijaya Prakash, and J. J. Baumberg, Appl. Phys. Lett. **86**, 041110 (2005).
[8] D. G. Lidzey, D. D. C. Bradley, T. Virgili, A. Armitage, M. S. Skolnick, and S. Walker, Phys. Rev. Lett. **82**, 3316 (1999).
[9] D. G. Lidzey, A. M. Fox, M. D. Rahn, M. S. Skolnick, V. M. Agranovich, and S. Walker, Phys. Rev. B **65**, 195312 (2002).
[10] S. Kéna-Cohen and S. R. Forrest, Phys. Rev. B **77**, 073205 (2008).
[11] R. J. Holmes and S. R. Forrest, Phys. Rev. Lett. **93**, 186404 (2004).
[12] R. F. Oulton, N. Takada, J. Koe, P. N. Stavrinou, and D. D. C. Bradley, Semicond. Sci. Technol. **18**, S419 (2003).
[13] J. Kasprzak, M. Richard, S. Kundermann, A. Baas, P. Jeambrun, J. M. J. Keeling, F. M. Marchetti, M. H. Szymanska, R. Andre, J. L. Staehli, V. Savona, P. B. Littlewood, B. Deveaud, and L. S. Dang, Nature **443**, 409 (2006).
[14] A. Amo, D. Sanvitto, F. P. Laussy, D. Ballarini, E. del Valle, M. D. Martin, A. Lemaitre, J. Bloch, D. N. Krizhanovskii, M. S. Skolnick, C. Tejedor, and L. Vina, Nature **457**, 291 (2009).
[15] P. G. Savvidis, J. J. Baumberg, R. M. Stevenson, M. S. Skolnick, D. M. Whittaker, and J. S. Roberts, Phys. Rev. Lett. **84**, 1547 (2000).
[16] M. Saba, C. Ciuti, J. Bloch, V. Thierry-Mieg, R. Andre, L. S. Dang, S. Kundermann, A. Mura, G. Bongiovanni, J. L. Staehli, and B. Deveaud, Nature **414**, 731 (2001).
[17] S. Kéna-Cohen and S. R. Forrest, Nature Photonics **4**, 371 (2010).
[18] V. M. Agranovich, M. Litinskaia, and D. G. Lidzey, Phys. Rev. B **67**, 085311 (2003).
[19] M. Litinskaya, P. Reineker, and V. M. Agranovich, J. Lumin **119–120**, 277 (2006).
[20] V. M. Agranovich and G. C. La Rocca, Solid State Commun. **135**, 544 (2005).
[21] V. M. Agranovich and Yu. N. Gartstein, Phys. Rev. B **75**, 075302 (2007).
[22] P. Michetti and G. C. La Rocca, Phys. Rev. B **71**, 115320 (2005).
[23] M. Litinskaya, P. Reineker, and V. M. Agranovich, J. Lumin **110**, 364 (2004).
[24] P. Michetti and G. C. La Rocca, Phys. Rev. B **77**, 195301 (2008).
[25] J. Chovan, I. E. Perakis, S. Ceccarelli, and D. G. Lidzey, Phys. Rev. B **78**, 045320 (2008).
[26] S. Ceccarelli, J. Wenus, M. S. Skolnick, and D. G. Lidzey, Superlat. and Microstruct. **41**, 289 (2007).
[27] C. Manzoni, D. Polli, and G. Cerullo, Rev. Sci. Instrum. **77**, 023103 (2006).
[28] C. Gadermaier, G. Cerullo, C. Manzoni, U. Scherf, E. J. W. List, and G. Lanzani, Chem. Phys. Lett. **384** (4–6), 251 (2004).
[29] H. Fidder, J. Knoester, and D. A. Wiersma, J. Chem. Phys. **98**, 6564 (1993).

[30]M. Van Burgel, D. A. Wiersma, and K. Duppen, J. Chem. Phys. **102**, 20 (1995).

[31]T. Virgili, L. Luer, G. Cerullo, G. Lanzani, S. Stagira, D. Coles, A. J. H. M. Meijer, and D. G. Lidzey, Phys. Rev. B **81**, 125317 (2010).

[32]G. M. Akselrod, J. R. Tischler, E. R. Young, D. G. Nocera, and V. Bulovic, Phys. Rev. B **82**, 113106 (2010).

[33]T. B. Norris, in *Confined Electrons and Photons*, edited by E. Burstein and C. Weisbuch (Plenum, New York, 1995), 503–521.