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Ultrafast single-molecule photonics: Excited state dynamics in coherently coupled complexes

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Abstract

We present a single-molecule study on femtosecond dynamics in multichromophoric systems, combining fs pump–probe, emission-spectra and fluorescence-lifetime analysis. The ultrafast fs approach gives direct information on the initial exciton dynamics after excitation. The lifetime data show superradiance, a direct measure for the extent of the coherent coupling and static disorder. The spectra finally reveal the role of exciton–phonon coupling. At the single-molecule level a wide range of exciton delocalization lengths and energy redistribution times is revealed.

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Keywords: Single-molecule detection; Pump–probe; Exciton delocalization; Superradiance; Exciton–phonon coupling

1. Introduction

The detection and visualization of individual molecules, once a dream, is today a common practice. Quantum phenomena, such as photon anti-bunching, molecular blinking and discrete photodissociation, molecular diffusion, rotation, interactions: all show up in full detail at the level of a single entity. Today the challenge is to exploit these achievements to build and control truly functional molecular wires, switches, etc. (often inspired by nature). This requires a multidisciplinary interplay between synthesizing and addressing the molecular systems. To track excited state dynamics it should be realized that most molecular interactions occur on ultrafast (fs–ps) time. Conventional fs–ps experiments have been restricted to large populations of molecules, until in 2004 we bridged the gap between "ultrafast" and "single-molecule" detection by a single-molecule pump–probe (SM2P) method [1]. We have applied SM2P to study both intra- and intermolecular fs dynamics of single quantum systems, revealing the importance of conformational heterogeneity and the influence of coherent coupling [1–3].

Ultrafast detection of single entities is particularly relevant for fs–ps energy transfer processes in complex systems, such as light harvesting complexes, some autofluorescent proteins, photonic polymers, etc. As a first step towards molecular wires we are studying chains of two, three and more chromophores, fabricated through both synthetic and biomolecular routes [4–7]. We have focused particularly on coherent strongly coupled assemblies, where we find longer femtosecond time response and discrete jumps in decay times, reflecting sudden change in coupling of the quantum coupled system. In this short contribution we report on ultrafast single-molecule

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detection of the trimer complex of the tetraphenoxy-perylene diimide chromophore (TPD) [3].

2. Unraveling disorder by ultrafast single complex detection

Coherent exciton delocalization in multichromophoric complexes reveals itself through superradiance and line narrowing. The extent of the exciton delocalization is generally limited by disorder, both static and dynamic [8,9], see Fig. 1. Static disorder is caused by differences in the energy of the interacting chromophores, which confine the initial exciton to a size smaller than the actual complex [8]. Subsequent coupling to molecular vibrations and phonon modes, i.e. dynamic disorder, reduces the coherence size of the exciton even further [9]. Thus the interplay between static energy disorder and dynamic phonon–exciton coupling constrains the extent of the final thermalized exciton, ultimately determining the spectro-temporal properties of the emitted photons [10,11]. One can disentangle the static disorder by addressing individual complexes, where each complex has its specific conformation and delocalization [12]. Moreover by combining ultrafast and spectral detection we can address both the initial and final exciton state for each selected complex.

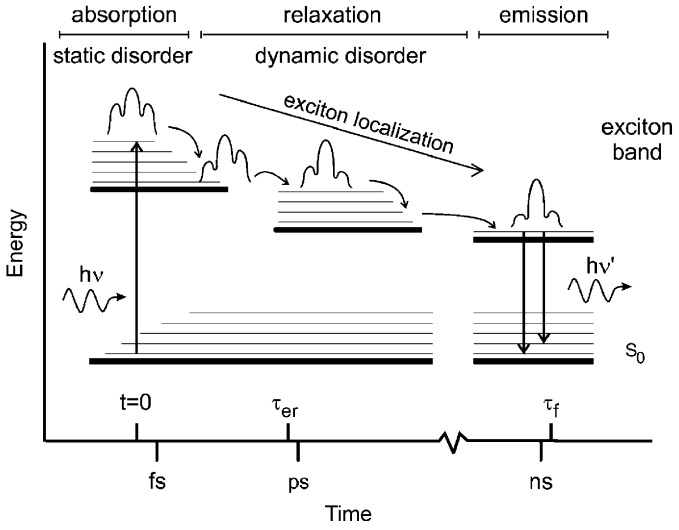

Fig. 1. Time evolution of excited state dynamics of a strongly coupled multichromophoric excitonic complex. On absorption an initial exciton ($t = 0$) is created with a delocalization length limited by static disorder, as depicted in the wavefunction sketch. The phonon-driven ultrafast dynamics leads to intraband energy relaxation, which reduces the coherence size of the exciton τ_{er}. The fs pump–probe experiment measures the onset of this process. The resulting thermalized exciton relaxes ultimately by fluorescence emission, with spectrum and lifetime τ_F depending on the final coherent delocalization length.

Single-molecule time traces of TPD complexes (Fig. 2(a)) reveal the occurrence of multilevel intensities, due to sequential photodamaging of the constituent chromophores in the complex [3,4] (Fig. 2(b)). The jumps in fluorescence intensity correlate with changes in fluorescence lifetime τ_F, e.g. 3.9 ns for the trimer, 4.9 ns for the left-over dimer to 6.5 ns for the last intact chromophore in Fig. 2(c); a clear signature of superradiance. Interestingly the lifetime ratios give a direct measure of the stepwise decreasing exciton delocalization length. Fig. 2(d) shows the effect of exciton delocalization on the sequential emission spectra of the trimer. Besides red shift of the 0–0 and 1–0 emission bands at $\lambda \sim 610$ and 660 nm, respectively, the vibronic component (1–0 band, indicated by arrow) becomes weaker due to decreased coupling between the electronic state and the vibrational mode [9].

The effect of coupling between electronic and vibrational degrees of freedom on the initial exciton is reflected in the ultrafast decay of the excited states. Fig. 2(e) shows the result of ultrafast probing of the sequential TPD levels.

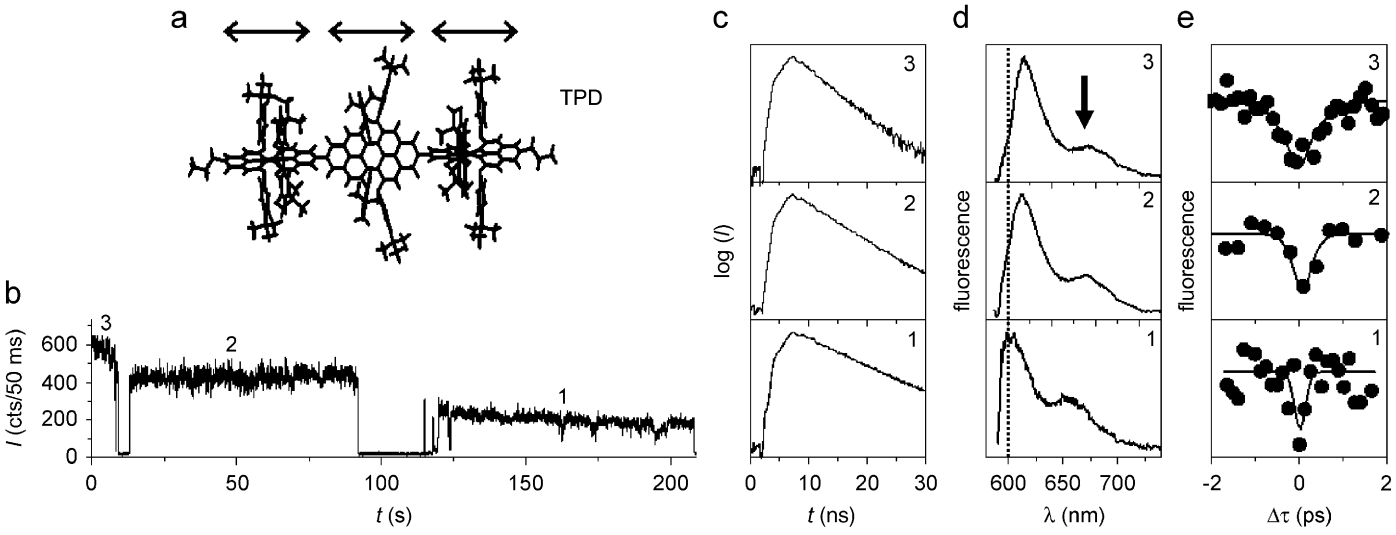

Fig. 2. (a) Optimal geometry of TPD calculated at the MNDO level by means of the Gaussian98 package, where arrows indicate the main transition dipole moment of the perylene diimide moieties. (b) Fluorescence transient of a single TPD complex showing sequential photobleaching [4] and dark intervals [5] of the chromophores (reflected in the stepwise signal levels 3, 2 and 1. (c) Fluorescence decay (lifetime), (d) emission spectra and (e) ultrafast SM2P dips for level 3, 2 and 1, respectively.

A clear dip in fluorescence intensity at zero pulse delay is visible while for $\Delta\tau > 0$, coupling to phonons leads to relaxation of the initially excited state and fluorescence is increased [1,2]. The width of the dip reflects the ultrafast energy redistribution time τ_{er}. The solid lines show fits which recover redistribution times of 380, 180 and 40 fs for the sequential levels of the particular complex shown. Interestingly, the redistribution time increases with the number of interacting molecules, indicating a decrease in phonon coupling efficiency on delocalization, consistent with the spectral data.

On addressing many trimer complexes (in the same sample) we observe a wide range of excitonic coupling strengths, as evidenced by the measured varying degree of superradiance. Despite the disorder, the single-molecule approach allows to reveal a clear correlation between the fs redistribution time and the extent of exciton delocalization [3].

3. Conclusions

We have presented femtosecond detection of single excitonic complexes, at room temperature. The intramolecular energy redistribution time increases with extent of the delocalization of the initial exciton. Ultrafast single-molecule detection will prove valuable to address photodynamics in complex systems, e.g. in molecular biology and molecular photonics.

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References

[1] E.M.H.P. van Dijk, J. Hernando, J.-J. García-López, M. Crego-Calama, D.N. Reinhoudt, L. Kuipers, M.F. García-Parajó, N.F. van Hulst, Phys. Rev. Lett. 94 (2005) 078302.
[2] E.M.H.P. van Dijk, J. Hernando, M.F. García-Parajó, N.F. van Hulst, J. Chem. Phys. 123 (2005) 064703.
[3] J. Hernando, E.M.H.P. van Dijk, J.P. Hoogenboom, J.-J. García-López, D.N. Reinhoudt, M. Crego-Calama, M.F. García-Parajó, N.F. van Hulst, Phys. Rev. Lett. 97 (2006) 216403.
[4] J. Hernando, J.P. Hoogenboom, E.M.H.P. van Dijk, J.J. García-Lopez, M. Crego-Calama, D.N. Reinhoudt, N.F. van Hulst, M.F. García-Parajó, Phys. Rev. Lett. 93 (2004) 236404.
[5] J.P. Hoogenboom, E.M.H.P. van Dijk, J. Hernando, N.F. van Hulst, M.F. García-Parajó, Phys. Rev. Lett. 95 (2005) 097401.
[6] J. Hernando, P.A.J. de Witte, E.M.H.P. van Dijk, J. Korterik, R.J.M. Nolte, A.E. Rowan, M.F. García-Parajó, N.F. van Hulst, Angew. Chem. 43 (2004) 4045.
[7] G. Sánchez-Mosteiro, E.M.H.P. van Dijk, J. Hernando, M. Heilemann, P. Tinnefeld, M. Sauer, F. Koberling, M. Patting, M. Wahl, R. Erdmann, N.F. van Hulst, M.F. García-Parajó, J. Phys. Chem. B. 101 (2006) 26349.
[8] H. Fidder, J. Terpstra, D.A. Wiersma, J. Chem. Phys. 94 (1991) 6895.
[9] F.C. Spano, J.R. Kuklinski, S. Mukamel, Phys. Rev. Lett. 65 (1990) 211.
[10] V. Chernyak, S. Mukamel, J. Chem. Phys. 105 (1996) 4565.
[11] D.J. Heijs, V.A. Malyshev, J. Knoester, Phys. Rev. Lett. 95 (2005) 177402.
[12] M. Lippitz, C.G. Hubner, T. Christ, H. Eichner, P. Bordat, A. Herrmann, K. Mullen, T. Basche, Phys. Rev. Lett. 92 (2004) 103001.