S_2 to S_1 Relaxation Dynamics in Perylene Bisimide Dye Aggregates and Monomers

Steffen Wolter[1], Franziska Fennel[1], Marco Schröter[1], Jan Schulze[1], Frank Würthner[2], Oliver Kühn[1], and Stefan Lochbrunner[1*]

1: Institut für Physik, Universität Rostock, Universitätsplatz 3, 18055 Rostock, Germany;
2: Institut für Organische Chemie and Center for Nanosystems Chemistry, Universität Würzburg, 97074 Würzburg, Germany
Author e-mail address: stefan.lochbrunner@uni-rostock.de

Abstract: The ultrafast relaxation from the S_2 to the S_1 state in perylene bisimides is investigated by femtosecond absorption spectroscopy. The relaxation takes place on a timescale of 150 fs and accelerates slightly upon aggregation.

OCIS codes: (320.7150) Ultrafast spectroscopy; (320.2250) Femtosecond Phenomena; (160.4890) Organic materials

1. Introduction

Exciton-Exciton annihilation has a strong impact on the exciton dynamics and the energy transport properties of organic supramolecular structures as well as of disordered molecular systems [1]. In an annihilation event two excitons encounter and merge on one chromophore leading to a highly excited electronic state S_n. So far, annihilation models assume that this state is very short living and the relaxation back to the single exciton band takes a negligible amount of time. Nevertheless, this assumption has to be proven as the relaxation from the S_n state is complex and multiple states and transitions might be involved. In this work, we address the relaxation from the S_2 state to the S_1 state of fourfold in bay area phenoxy-substituted perylene bisimides, which are popular building blocks for supramolecular structures [2], and study the influence of aggregation on this process. Two slightly different perylene bisimide molecules with the same chromophore but different substituents at the R2 position (see Fig. 1c) are investigated. PBI 1 includes a hydrogen bond donating subunit resulting in efficient and stable J aggregation in methylcyclohexane (MCH) [3] while PBI 2 exists as monomers in MCH.

2. Experimental Approach

Transient absorption measurements are performed by exciting the sample with a tunable pump pulse delivered by a noncollinear optical parametric amplifier and probing it by a CaF_2 white light continuum. The white light is compressed by a prism sequence to obtain a high time resolution and to minimize artifacts around time zero. We selectively excite either the S_1 state (Fig. 1a) by means of a 545 nm pump pulse or the S_2 state (Fig. 1b) at 440 nm to observe the impact of the S_2-S_1 relaxation.
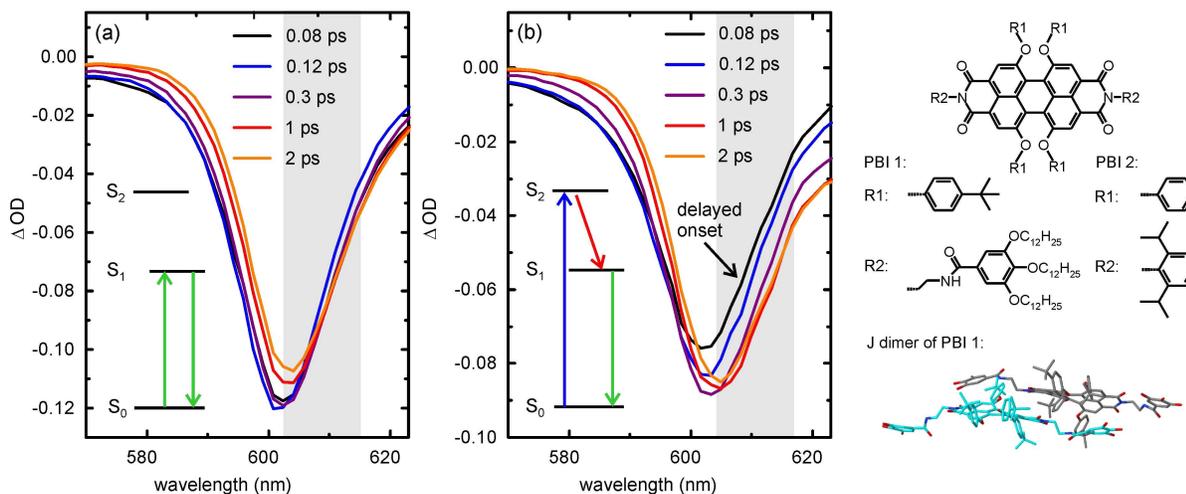

Figure 1: Transient spectra of PBI 1 aggregates in MCH after excitation to the S_1 state (a) and to the S_2 state (b). In the case of S_2 excitation a delayed onset of the stimulated emission from the S_1 level is observed. c) Molecular structures of PBI 1, PBI 2, and J dimer representing the basic structure of PBI 1 aggregates.

In the case of S_1 excitation of PBI 1 aggregates (Fig. 1a) the dynamics in the first 2 ps mainly reflects intramolecular vibrational redistribution (IVR), manifested by a slight shift of ground state bleach and stimulated emission. In the case of S_2 excitation (Fig. 1b) the ground state bleach in the spectral region of the S_1-S_0 absorption is again present from time zero on and the transient absorption below 605 nm, which is dominated by this contribution, exhibits only minor changes with time. In contrast, above 605 nm an additional signal increase within a few hundred femtoseconds is observed. In this spectral region the stimulated emission from the S_1 state contributes strongly to the transient signal. It only appears after the population of the S_2 state has relaxed to the S_1 state, most probably via a conical intersection, and thus its delayed rise gives the relaxation time from the S_2 to the S_1 state.

3. Analysis of the Dynamics

In Figure 2a) time traces in the spectral region of the ground state bleach and the stimulated emission from the S_1 state are displayed for the PBI 1 aggregate and the PBI 2 monomer. To extract the time constants of the S_2-S_1 relaxation the traces are fitted with an exponential decay and the signal onset with an error function.
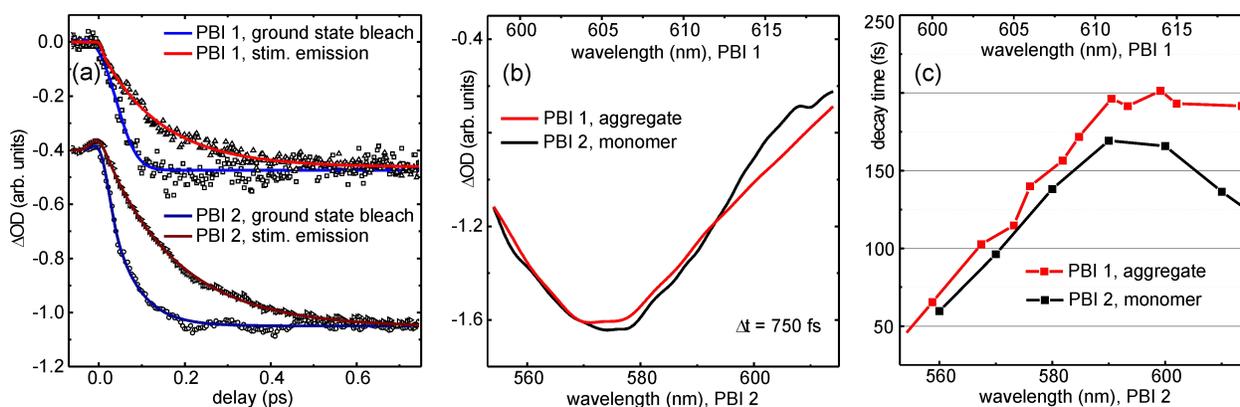

Figure 2: a) Time traces for PBI 1 aggregates and PBI 2 monomers after S_2 excitation at characteristic wavelengths in the region of the ground state bleach and the stimulated emission of the S_1 state. b) Transient spectra at a delay time of 750 fs. The top and bottom x-axis belong to PBI 1 (red) and PBI 2 (black) respectively and are scaled in order to match the band positions and widths of the dominant transient bands. c) Time constants of the fast signal component for PBI 1 (red) and PBI 2 (black). The wavelength axes are scaled according to (b).

For a fair comparison of the relaxation behavior in PBI 1 aggregates and PBI 2 monomers one has to take into account that the width and exact spectral position of the bleach and stimulated emission depend somewhat on the molecule and the aggregation state. To this end, the wavelength axes are scaled in such a way that the dominant transient bands of both compounds, which are caused by bleach and stimulated emission, are on top of each other after the fast processes are over (see Fig. 2b). Figure 2c) shows a comparison of the extracted time constants which exhibit a distinctive wavelength dependence prohibiting a global fit. We attribute this wavelength dependence to the superposition of two fast processes, namely S_2-S_1 relaxation and IVR. In the spectral region of the ground state bleach the decay dynamics are dominated by IVR processes and only slight differences between PBI 1 aggregates and PBI 2 monomers are observed. In the region around 612 nm (590 nm), the transient absorption signal of the PBI 1 aggregates (PBI 2 monomers) is to a large extent due to stimulated emission and thus, the observed decay should mainly reflect S_2-S_1 relaxation. In both cases this process takes about 150 fs to 200 fs. However, for the aggregated compound the observed time constants are systematically longer than for the monomer and aggregation seems to slightly slow down the depopulation of the S_2 state. Interestingly, the stationary absorption spectra show a small increase of the energy gap between the S_2 and S_1 state upon aggregation indicating that, in accordance with the energy gap rule, a larger energetic separation is associated with a slower relaxation rate. Aggregation seems to influence the relaxation of higher electronic states and thereby also the speed of the deactivation step in exciton-exciton annihilation.

4. References

[1]   S. Wolter, J. Aizezers, F. Fennel, M. Seidel, F. Würthner, O. Kühn, and S. Lochbrunner, *New J. Phys.*, 2012, **14**, 105027.
[2]   F. Würthner, *Pure Appl. Chem.*, 2006, **78**, 2341–2349.
[3]   F. Fennel, S. Wolter, Z. Xie, P.-A. Plötz, O. Kühn, F. Würthner, and S. Lochbrunner, *J. Am. Chem. Soc.*, 2013, **135**, 18722–18725.